Corrosion

IN THIS ISSUE:

ALSO: Latest News About Programs for
NACE Regional Meetings This Fall

CORROSION CONTROL

NATIONAL ASSOCIATION
OF CORROSION ENGINEERS

Tex.

This Month in Corrosion Control . . .

SULFITE PAPER MILL environments require corrosion resistant materials of high integrity. Experience data on numerous stainless steels in the environments common to pulp mills are given beginning on Page 9.

CALCIUM SULFATE SCALE is a prime culprit in the corrosion of stainless steel pulp digesters. Among remedial procedures were changes in operations and improvements in scale removal equipment. Turn to Page 15.

STAINLESS STEEL OVERLAYS in Kraft digesters are thoroughly discussed in an article beginning on Page 20. Details of overlay procedure, repair methods, types of rods and other significant information are included. Tests to locate preferred procedures are underway.

VAPOR AREAS in pulp digesters, often the most difficult to protect from corrosion, may be amenable to cathodic protection. An interesting proposal about a system designed for digesters is included in a discussion beginning on Page 26.

NACE REGIONAL MEETING programs are fast rounding into shape. Turn to NACE News, Page 51, for the most recent information on these programs to be held in October, November and December. Also included are notices of scheduled section meetings in various parts of the country. Keep up with association events by reading this section monthly.

STEEL CORRODES faster when exposed to high-energy ultraviolet light than it does when not lighted; a mixture of visible and infrared light apparently results in less corrosion than is caused by infrared alone. Turn to Page 93.

HIGH PURITY WATER out-of-reactor environments cause less corrosion of carbon and low alloy steels when pH is 7 than when it is less than 10, research reported in an article beginning on Page 95 indicates. Corrosion rates for all carbon and low-alloy steels were higher than for AISI Type 300 stainless.

IRON-ALUMINUM ALLOYS, because of their good performance in systems subjected to hydrogen sulfide and oil ash corrosion, are surveyed in a study beginning on Page 103. Advantages of aluminum additions are considered. Numerous data on Russian practice, phase diagrams and comparisons with other materials are given.

INHIBITIVE EFFECT of acetylenic alcohols used with aqueous mineral acids for oil well acidizing, acid cleaning and pickling is described in an article beginning on Page 109. Comparisons are made among data derived from laboratory tests of the alcohols and commercial inhibitors. Mechanism of the effect is explained.

WHY DO WASH PRIMERS lose adhesion with time? Turn to Page 114 for a thorough examination of this phenomenon, structure diagrams, reaction diagrams, for the familiar WP-1 surface conditioner.

BACTERIAL CORROSION of iron, which has been receiving increasing attention during the past 10 years in this country, long has been a matter for intensive study in some European countries. Notable among the early workers in this field was C.A.H. von Wolzogen Kuhr, who, as head of a research program in Holland wrote and presented his classical paper "Unity of Anaerobic and Aerobic Iron Corrosion of Soil," at the Fourth National Bureau of Standards Soil Corrosion Conference in 1937. Copies of this paper are rare. Editors of CORROSION welcome the opportunity to reprint this work for scientists concerned with this problem. Turn to Page 119.

UNDERGROUND POWER CABLES CORRODE if they are not protected. A review of the methods and devices used in the Cleveland area begins on Page 126. A novel reverse current switch is described, new types of rectifiers and the use of silicon diodes in the protective systems illustrated.

SALT CONTAMINANTS have a marked effect on the corrosion rates of superalloys at high temperatures. Data on five materials exposed to potassium chloride and lithium fluoride are given in an article beginning on Page 131.

CHLOROSULFONATED POLYETHYLENE'S physical and chemical properties are described in a report of NACE Technical Committee T-6A beginning on Page 139. General comments on chemical resistance are included, and ratings against about 350 corrosives and corrosive environments are given in tabular form.

ATMOSPHERIC CORROSION tests on a number of ferrous and non-ferrous metals and alloys are reported in an article beginning on Page 144. Environments were rural, industrial, marine-industrial, marine, far northern and semi-industrial.

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DISCUSSIONS

Top guns in your anti-corrosion arsenal

When you're waging your battle against corrosion, it will pay you to have DeVilbiss spray guns for full covering coatings that provide greater protection on any surface—flat, recessed, irregular or angular. Application is far faster than any contact application method.
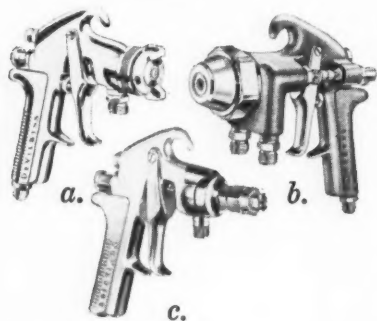
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INDEX TO ADVERTISERS

Corrosion Control Measures and Water Pollution Control

INCREASINGLY HEAVY DEMANDS are being made on the supply of water available for industrial use. In some sections, supplies are so limited that industries are using effluent from sewage plants. In others, growing populations demand an ever-increasing share of the available supply, and because uses for people have higher priority than uses for industry, large scale users are looking at their operations with the view of reducing consumption.

The obvious answer in many cases is recirculation. This alternative also becomes attractive when the delivered price of water makes once-through use uneconomical, even when the supply is adequate.

With recirculation come the troubles of scale, algae, materials deterioration, diminishing heat transfer rates, esthetic and property damage problems as well as safety hazards from blow-down, and a number of others well known to the engineers that maintain the heat exchangers.

Many difficulties associated with the operation of cooling towers have been solved in whole or part. Technical committeemen working in the NACE have considered, tested and experimented with various solutions and have selected from those available those which meet the needs of their respective installations. It is true, however, that no final over-all solution of these problems has been found, nor will the solution applied to one installation always give good results in another.

The question of pollution of river systems by wastes from municipal sewerage systems is now being acrimoniously considered in suits between the Public Health Service and several cities. Exactly how much power the federal government has to compel pretreatment of wastes before discharge into waterways remains to be established by judicial decision.

Futhermore, widespread action against industries by local political subdivisions to control pollution of water is growing and probably will continue to grow as new laws are passed.

In another connection, the federal government, the states and local political subdivisions have been active and largely successful in controlling the discharge of salt water produced by oil wells into streams and underground where they may contaminate fresh water aquifers.

All of these activities—and the reasonable assumption that activity will increase in frequency, intensity and success as time goes on—point to the necessity for industry to find means of avoiding difficulties. Industries also are involved sometimes when a conflict arises between the federal government and a municipality over the disposition of municipal effluent into interstate waterways.

Better recirculating practices and application of known methods of controlling the corrosion ills that beset cooling towers and other heat exchangers will materially reduce the cost of maintaining adequate water for industrial use. Furthermore, there are solid economic reasons for scientifically attacking the corrosion problems associated with heat exchangers involving water.

Even in the end-treatment of industrial wastes, considerable corrosion problems exist. Often, standard bacteria treatment is futile, other methods must be used to clean water before discharge. Because most of these involve concentration and separation of the wastes by one method or another and because concentrated wastes are corrosive, special control measures are necessary.

It is hoped that more attention will be paid to the corrosion control aspects of the water pollution problem so that expensive mistakes can be avoided.

How to choose a metal for <u>high-temperature</u> service

In every sense, "the heat's on" and "the pressure's on" when metals go to work at high temperatures. The basic trend in processing equipment has been toward higher pressures, higher temperatures, and more corrosive conditions.

That's why questions like these are being asked today: What metal is used within the core of a gas-cooled reactor where operating temperatures go up to 1700°F? What metal is used for the "skin" of a missile that must take supersonic heats from 400° to 600°F ... and be the structural framework for 130 tons of dead weight? What metal is used to withstand the corrosion of hot ammonia gas at 900°F? What metal is used for strength and corrosion resistance above 1000°F?

The answer, in each case: Nickel Stainless Steel.

Nickel works as a strengthening and toughening agent. In steel it promotes the formation of austenite, which is stronger and more stable at high temperatures than ferrite. Nickel steps up steel's resistance to oxidation, carburizing, nitriding and thermal fatigue.

The war against corrosion. High-temperature equipment is exposed to a great many different atmospheres and corrosive conditions. Many materials coming from high-temperature processing and handling must be delivered uncontaminated by the products of corrosion. Nickel stainless steels are especially good for fighting corrosion ... perform well under those oxidizing conditions harmful to unalloyed steel. The stainless steels possess the ability to protect themselves with oxide films that form a shield against corrosion. And *stainless* steel, as the name implies, stays brighter, cleaner ... and the protective "oxide layer" is less likely to be broken or reduced by pitting or scaling.

What strength means at high temperature. By a mechanism known as "creep" metals at elevated temperatures flow plastically though subjected to stresses below their yield strength, as determined by short-time tensile tests. The creep strength of nickel stainless

steels is an important reason for their increasing use in a variety of high-temperature operations. Both *time* and *stress* are design factors at high temperatures. The most generally useful data are those for creep and rupture—one or the other is the basis for most allowable stress values in design work.

The chart below gives the creep and rupture strength data of two nickel stainless steels that have found wide acceptance in high-temperature service:

AISI TYPE	CREEP STRENGTH			
	1000°F		1500°F	
	1% 100,000 hrs,psi	1% 10,000 hrs,psi	1% 100,000 hrs,psi	1% 10,000 hrs,psi
310	17,500	32,500	1,250	3,500
316	14,750	24,500	1,800	4,200

AISI TYPE	RUPTURE STRENGTH			
	1000°F		1500°F	
	100,000 hrs,psi	10,000 hrs,psi	100,000 hrs,psi	10,000 hrs,psi
310	21,000	25,000	1,600	2,800
316	––	––	1,600	3,400

Don't stop at creep and rupture strength ... other critical questions must be considered in the selection of metals for high-temperature service. They include:

- high temperature ductility
- short-time tensile properties to help evaluate resistance to momentary overloads
- thermal shock resistance

Before selecting a metal for a specific service ask yourself these questions:

☐ What is the maximum temperature of operation?

☐ What kind of temperature cycling will occur?

☐ What maximum load will be encountered? Will it be constant or cyclic?

☐ What types of atmosphere or other corrosive conditions?

☐ What size or shape of the parts or sections?

☐ What further processing will be done, such as welding or machining?

☐ What abrasive or wear conditions will be encountered?

The nickel stainless steel family can serve you in a wide range of high-temperature operations. That's why it's best to bring your metal problem to Inco's High Temperature Engineering Section. They are fully prepared to give you practical answers on the metal that will work best in your application. A note to Inco will bring you the "High Temperature Worksheet" to guide you in describing your metal problem.

LITERATURE

The publications listed below will provide more detailed information on choosing metals for high-temperature service.

PUBLICATION NUMBER	NAME
A266	Heat Resistant Castings, Corrosion Resistant Castings ... Their Engineering Properties and Applications
A227	Stainless Steel for Pressure Vessels
	High Temperature Corrosion in Refinery and Petrochemical Service
A164	Thermal Expansion Characteristics of Stainless Steels Between −300°F and 1000°F
A248	Compilations of Chemical Compositions and Rupture Strengths of Super-Strength Alloys

A complete listing of Inco publications and technical bulletins can be obtained by writing for "List A" to:

The INTERNATIONAL NICKEL COMPANY, Inc.

67 Wall Street INCO New York 5, N. Y.

Figure 1—Type of rod used to obtain corrosion data. Letter A: Test rod and bolts fabricated from material known to have sufficient resistance for duration of test. Letter B: Standard specimens were 1½-inch diameter by 3/16-inch thick, insulated with Teflon. Letter C: Flange diameter dimensions were same as raised face dimensions for flanges (ASA B16e).

TECHNICAL TOPICS

Abstract

Allowable corrosion rates for equipment with low corrosion tolerance are discussed. Corrosion case histories in the various pulping processes are presented. Sulfite pulping solutions are most frequently handled in 316 material. Stainless 316 is used because of good resistance to local attack under scale or deposits.

In alkaline pulping, soda process digesters are usually made of carbon steel with heater tubing of either carbon steel or Type 316 alloy. Kraft digesters are commonly carbon steel, though many units are partially to wholly lined with alloy materials, Type 316 most frequently. Stainless 316 is used for heater piping, strong black liquor piping and green liquor piping. Carbon steel is most frequently used for weak black liquor.

Corrosion in groundwood pulping varies greatly depending on wood being ground, water supply and treating chemicals added. Stainless 304 and 316 alloys are used frequently, both to resist corrosion and reduce contamination.

Chlorine and hypochlorite bleaching usually pose severe corrosion problems. Hastelloy C alloy is most commonly used for high strength solutions. In more dilute solutions the molybdenum-bearing stainless steels are satisfactory. Chlorine dioxide is even more corrosive to metals than hypochlorite, and some operators have replaced Hastelloy C with titanium.
8.5.3

Introduction

SULFITE PULP MILLS were among the earliest users of austenitic stainless steels for valves and fittings to handle cooking acid. Corrosion information was very limited in the early days and it became obvious that a real service could be rendered by making available to the industry simply-used corrosion test rods. Figure 1 illustrates the type of rod used to obtain the data presented here. Because valves are the primary interest of the author's company, it was desirable to locate the samples in the piping where conditions closely approach those to which a valve is exposed. The rod can be placed easily between the mating flanges of any line two inches in diameter or larger. The rod also can be made for exposure in a vessel, tank or location other than a pipe line.

★ Revision of a paper titled "Corrosion of Stainless Steels and Higher Alloys in Pulp Mill Operations" presented at a meeting of the Southeast Region, National Association of Corrosion Engineers, Jacksonville, Fla., October 2, 1959.

Allowable corrosion rates of valve materials must of necessity be lower than those permissible for piping or vessels, because seating surfaces must retain their integrity. Experience indicates that a maximum corrosion rate of .005 ipy without pitting and crevice corrosion, must not be exceeded to assure reasonable valve life.

Alloys of primary concern are shown in Table 1. A valve for corrosive service normally is built with all wetted components of the same alloy and with an integrally cast seat to eliminate the crevice between seat ring and body which always is a potential source of failure.

In making pulp, several well established methods are in use. Each has certain inherent characteristics which are outside of the scope of this discussion. These methods are (1) sulfite-calcium, magnesium, sodium and ammonium base, (2) alkaline-soda and

Review of Some Data on

Corrosion

of

Stainless Steel

and

Higher Alloys

in

Pulp Mill

Equipment*

Harold C. Templeton

Alloy Steel Products Company
Linden, New Jersey

For other articles on
**PULP DIGESTER
CORROSION CONTROL**
See Pages 14, 20 and 26.

TABLE 1—Alloy Composition Data

Alloy	Nominal Composition, Percent								
	C	Cr	Ni	Mo	Cu	Mn	Si	W	Fe
CF-8 (304)	.07	19.0	9.5	....	...	.85	0.90	..	...
CF-8M (316)	.07	19.0	11.0	2.5	...	.85	0.90	..	...
CN-7M (Alloy 20)	.07	20.0	29.0	2.5	4.0	.75	1.00	..	...
CG-8M (317)	.07	20.0	11.0	3.25	...	.85	0.90	..	...
Monel	.10	...	67.0	....	30.0	.75	1.25	..	1.50
Nickel	.20	...	97.0	....	...	..	1.50	..	0.50
Ni-Mo (Hastelloy B)	.07	...	Bal.	28.0	...	.85	1.00	..	6.00
Ni-Mo-Cr (Hastelloy C)	.10	16.0	Bal.	16.0	...	.75	0.90	4.5	5.00
Ni-Cr-Fe (Inconel)	.15	13.5	77.5	....	...	.80	1.25	..	6.00

Pulp Mill Equipment –

(Continued From Page 9)

kraft, (3) semi-chemical and (4) mechanical or groundwood.

After completion of the pulping process, a bleaching operation usually is used to remove coloring in the fibers to produce pulp of desired brightness.

Bleaching methods are (1) chlorine-hypochlorite, chlorine dioxide, hypochlorous acid and sodium chlorite, (2) peroxide and (3) bisulfite and hydrosulfite.

Paper making operations are not included in this discussion.

Sulfite Pulping Systems

Sulfite cooking liquor or cooking acid is a bisulfite liquor base in a sulfurous acid solution. The base may be calcium, magnesium, sodium, or ammonium.

Table 2 shows neglible corrosion rates and no local attack on stainless steel materials in calcium bisulfite cooking acid at 150 F. Table 3 gives rates in a similar solution at 284 F. Weight loss corrosion rates are insignificant. No local attack was noted.

Calcium Bisulfite Liquors

Teeple[1] reporting on corrosion tests in calcium bisulfite cooking liquors, points out that weight loss corrosion rates indicate that Type 304 (18-8) is suitable. He further cites experience showing that 304 material is not sufficiently resistant to localized attack to justify its use and that Type 316 should be selected. Type 316 is especially required if much SO_3 is present, or if scale formation is appreciable. These considerations have led to virtual standardization of Type 316 for handling

TABLE 2—Digester Pulp and Sulfite Acid Mixture, 150 F Maximum, 1368 Hours

Alloy	Penetration mpy	Remarks
CF-8N (316) CN-7N (Alloy 20) Worthite	0.0	Light coating, no evidence of attack.

TABLE 3—Pulp Solution Plus 5 to 6 Percent Sulfur Dioxide, 284 F, 1656 Hours

Alloy	Penetration mpy	Remarks
CF-8M (316) CF-8 (304) CN-7M (Alloy 20) Worthite	0.5 0.7 0.5 0.7	Bright and clean. No attack.

TABLE 4—Green Liquor in Transfer Line from No. 1 Dissolver, 257 F, 6360 Hours*

Alloy	mpy	Remarks
CF-8 (304) CF-8M (316) CN-7M (Alloy 20)	0.0	Surface bright and clean with no evidence of attack.
Monel	0.1	Surface very lightly tarnished, otherwise no evidence of attack.
Ampco 18	....	Lost during exposure.
Mild steel	3.7	Surface moderately etched with no evidence of localized attack.
Ni-Resist No. 1 Ni-Resist No. 2	8.5 8.8	Surface heavily etched with no evidence of localized attack.

TABLE 5—Sodium Sulfide in Loading Line, Atmospheric Temperature, 6360 Hours**

Alloy	mpy	Remarks
CF-8 (304) CF-8M (316) CN-7M (Alloy 20)	0.0	Surface bright and clean, with no evidence of localized attack.
Monel	0.3	Surface tarnished plus some black adherent scale. Exposed area lightly etched with no evidence of localized attack.
Ampco 18 Carbon steel	35.9 20.8	Very heavily attacked.
Ni-Resist No. 1 Ni-Resist No. 2	3.8 5.4	Exposed surface very heavily etched with no evidence of localized attack.

TABLE 6—Sulfite Cooking Liquors in No. 2 Chemiground Wood Digester, 275 F, 1584 Hours

Alloy	mpy	Remarks
CF-8 (304) CF-8M (316) CN-7M (Alloy 20)	0.0	Bright and clean, no evidence of attack.
Carbon steel	0.4	Heavy black coating, moderate to heavy etch.
5% Phos. bronze	77.6	Heavy black coating, very heavy attack.
CF-8 (304) welded and heat-treated	0.0	Bright and clean, no evidence of attack.
CF-8 (304) as welded	0.0	
Ampco 18	84.0	Heavy black coating, very heavy attack.

TABLE 7—Pulp Grinder Stock (5-6% concentration, before main addition of zinc hydrosulfite brightening treatment) Located in Outside Grinder Dam on Grinder Pit, 170 F With Good Aeration and Agitation by Continuous Flow of Stock Over Specimens[6]

Alloy	Penetration mpy	Remarks
Monel	7	0.001 maximum pit.
Nickel	25	0.001 maximum pit, 0.001 maximum pit under spacer.
Inconel	0.3	0.013 maximum pit, 0.003 maximum under spacer.
Type 304	<0.1	0.007 maximum pit, 0.007 maximum under spacer.
Type 302	<0.1	0.004 maximum pit, 0.003 maximum under spacer.
Type 316	<0.1	
Carbon steel	34	0.001 maximum pit.
3½% Ni steel	48	0.001 maximum pit, 0.002 maximum under spacer.
5% Ni steel	43	0.003 maximum pit.
Cast iron	45	
3% NiCast iron	51	0.003 maximum pit, 0.001 maximum under spacer.
Ni-Resist	38	
Copper	13	

TABLE 8—Groundwood Decker Feed, Consistency About 0.6%, pH 4.4 to 4.7, 69 F Average, Agitation—Free Rapid Flow, 35 Days[6]

Alloy	mpy	Remarks
Monel	11	
Nickel	Missing	
Inconel	<0.1	0.018 maximum pit, 0.001 maximum under spacer.
Type 302 Type 304 Type 316 Type 309	<0.1	
Type 430	0.5	Hole, 0.026 maximum under spacer.
Carbon steel	46	
Cast iron	29	
Ni-Resist No. 2	32	
Phos. bronze	12	

TABLE 9—Bleach Liquor (35½ grams per liter chlorine, ½ gram per liter calcium oxide), 150 F Maximum, 3 Weeks

Alloy	mpy	Remarks
CN-7M (Alloy 20)	3.1	Surface bright and clean. Solution cell corrosion under Teflon insulating washer.
CF-8M (316)	19.1	Surface bright and clean. Solution cell corrosion under Teflon insulating washer more severe than on Aloyco 20.
Monel	188.2	Very heavy solution cell corrosion over one entire side and partly over other side.
Ni-Mo (Hastelloy B)	466.0	Very heavy pitting and solution cell corrosion over entire specimen.
Ni-Mo-Cr (Hastelloy C)	0.0	Bright and clean, with only very slight indication of solution cell corrosion under Teflon washer.

* All specimens had very heavy crystalline deposit 1/32 to 1/16 inch thick after exposure.
** All specimens when returned had a very heavy crystalline deposit 1/8 to 1/4-inch thick.

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calcium base liquors where welded fabrication is not involved, and of 316L if welding is used.

Magnesium Bisulfite Liquors

Cooking liquors using other bases than calcium have been of considerable interest in recent years. There are fewer corrosion data on magnesium bisulfite liquors than on the calcium base liquors. Data available appear to indicate that magnesium base liquors may be more corrosive than calcium base.

Kolberg[2] reports on corrosion encountered in a magnesium base sulfite mill at Ketchikan, Alaska. This report says high chloride contents were found in the closed acid recovery system. The chlorides which came from salt absorbed by water-borne logs contributed to the pitting corrosion of 316 alloy. When corroded normal analysis 316 equipment was replaced with 316 material containing 2.75 percent minimum molybdenum, the problem was solved. It was further pointed out that difficulties were encountered in some 316 parts which were below the 2.0 percent minimum molybdenum requirement. No specific corrosion rates were reported by Kolberg.

Teeple[1] also reported on tests in vapors from magnesia base pulping. These indicated that pitting and localized attack would be of considerable concern on Type 316, whereas Type 317 was free from local atttck and showed little overall corrosion. Teeple further said that some failures of Type 316 material have occurred in magnesium bisulfite mills.

Ammonium Bisulfite Liquors

Corrosion characteristics of ammonium bisulfite cooking liquors apparently are the same as those of calcium bisulfite liquors. Mills converted from calcium base to ammonium base report no corrosion problems as a result of the change. The use of sodium base liquors has not been explored on a large scale so far, but data available indicate that the material selections valid for calcium base liquors also can be applied to sodium base sulfite mills.

Alkaline Processes

The soda process uses a solution of caustic soda or soda ash plus a small amount of sulfur present as sodium sulfide. Corrosion problems usually are not severe and carbon steel is commonly used for digesters. The type of wood cooked affects corrosion rates, probably because of organic acids released, and in some cases severe corrosion has been encountered. Liquor heaters are commonly of carbon steel, although in some cases alloyed materials are required. La Que and Clarke[3] cite the use of Inconel in soda pulp and kraft process heaters where carbon steel tubing failed quickly.

The kraft process (sulfate) is considerably more corrosive than the soda process, even though solutions are somewhat similar. This is probably because of the higher sulfidity of kraft solutions. Digesters have been made of carbon steel, but recently many units have been constructed with corrosion resistant linings of austenitic stainless steels or of Inconel. Weight loss corrosion rates of austenitic stainless steels make them suitable for use, but they sometimes are subject to stress corrosion cracking.

Accumulation of concentrated alkaline liquors in crevices can lead to trouble. Despite this shortcoming, many units with stainless lined digesters are operating satisfactorily. Inconel also is suitable

Stainless Steel • • • • • • • • • • • • • •

(Continued From Page 11)

for digester linings, does not suffer from stress cracking and has been used satisfactorily.

Teeple[1] cited the results of a number of corrosion tests in sulfate pulp digestion. Corrosion rates on carbon steel ran as low as 0.6 mpy to a high of 95 mpy. Austenitic stainless steels and Inconel show acceptably low rates. The wide range in corrosion rates on carbon steel illustrate the fact that attrition of materials varies greatly from one installation to another.

Black liquor evaporation and chemical recovery are essential to economical operation of a kraft process mill. Allen[4] cites the need for 316 piping on liquor side of the first one or two stages of evaporators. He suggests that valves for concentrated liquor should be all 316, Ni-resist or 3 percent nickle iron with stainless trim.

Kraft green liquors do not pose unusual corrosion problems and normally are handled in 316 alloy piping and valves. Table 4 illustrates typical corrosion rates in green liquor. Crystalline deposits from the liquor can pose problems in equipment such as valves, because they may damage seating surfaces or otherwise interfere with their operation.

The handling of sodium sulfide poses no particular corrosion problems as illustrated by the rates in Table 5. Austenitic stainless steels are suitable.

Kraft Continuous Pulping

Corrosion in continuous digestion of pulp would not be expected to differ materially from that found in batch operation. One continuous pulping system in use in this country has been based on the kraft process, on units constructed domestically up to this time. Hydraulic pressure is used in the digester and no vapor space exists. Absence of a vapor phase in a continuous operation results in a corrosion rate so low that a carbon steel digester can be used.

For handling cooking liquor above 250 F, either 304 or 316 austenitic stainless steels have been found necessary to avoid corrosion problems. Handling strong liquor at any of the temperatures encountered require the use of 304 or 316 for equipment with low corrosion tolerance.

There are no specific corrosion data for this process, but the following examples illustrate the material selection problems.

Valves Failed in Six Months

1. A control valve of cast steel handling strong liquor at 180 F was corroded through body walls in approximately six months. This carbon steel valve was used instead of a stainless steel one which could not be obtained quickly. The replacement stainless valve has suffered no corrosion damage.

Shut-Off Valve Corroded Through

2. A cast steel shut-off valve after the blow valve corroded out in one installation through the body wall. This shut-off valve is now specified of austenitic stainless steel. This valve is located at the point where vaporization begins in the digester blowing process.

To summarize, alkaline processes usually involve material selections as follows:

Soda Process: digesters—carbon steel; heater tubing—carbon steel, 304 or 316 stainless steel and some Inconel.

Kraft: digesters—older units generally carbon steel, many recent units are stainless lined (316), some Inconel lined; heaters—304 and 316 stainless steel; black liquors—carbon steel in dilute liquors, concentrated liquors 316. For valves and pumps, 316, special alloys such as Worthite or 20 alloy and Ni-Resist. Green liquors—304, 316, 20 alloy and Monel.

Semi-Chemical Pulping

The combination of chemical digestion of certain grades of wood for pulp in conjunction with disc type refining or other methods of fiberizing has become fairly widely used. The various semichemical pulping processes are as follows: (1) neutral sodium sulfite (2) kraft semi-chemical (3) cold caustic and (4) chemiground wood.

Neutral sodium sulfite semi-chemical pulping uses a liquor prepared in much the same way as acid sulfite. This liquor is buffered to maintain a nearly neutral pH during the cook cycle.

Murtfeldt[8] reported on corrosion in a neutral sodium sulfite semi-chemical mill, where digesters were stainless steel fitted and acid brick lined. The stainless steel showed no corrosion. In the liquor plant, cast-iron pumps graphitized and were replaced with Ni-Resist. Digester relief piping of carbon steel and piping for circulation during dilution corroded and replaced with 316 piping. Cast Iron white liquor pumps failed from corrosion in one year.

Corrosion in neutral sodium sulfite cooking liquor appears to be of the same magnitude as that encountered in acid sulfite liquors. Alloy or acid brick-lined digesters may be required. In the cooking liquor plant 316 alloy or special austenitic stainless steels of the 20-type appear to be suitable.

Kraft Semi-Chemical Systems

Corrosion in kraft semi-chemical pulping operations does not appear to vary significantly from that which is encountered in straight kraft chemical pulping. Material selections applicable for kraft chemical pulping appear to be valid for kraft semi-chemical pulping also.

Cold Caustic Systems

Cold caustic semi-chemical pulping is a recent development of the Forest Products Laboratory. Because of the solutions handled, corrosion problems should be very minor and probably all pulping solutions can be handled in steel or low alloy equipment.

Chemigroundwood Systems

The chemigroundwood pulping process operates by treating billets of wood in a pressure vessel before grinding. Racks of wood are placed in a treating chamber, following which a 28-inch mercury vacuum is drawn on the vessel. Treating liquor, six parts of sodium sulfite to one part of sodium bicarbonate is then drawn into the vessel with air excluded.

The digester is then heated to between 275 F and 302 F. A pump then raises

• • • • • • • • • • • Pulp Mill Equipment

the hydrostatic pressure from 100 to 150 psig by pumping liquor from the storage tank into the digestion vessel. This temperature and pressure are maintained for several hours, after which the liquor is blown into an accumulator. The billets are then moved from the vessel to the grinder room for grinding. Test results in Table 6 were obtained on cooking liquors being handled in a chemigroundwood digester.

Corrosion encountered in this cooking solution does not seem to differ appreciably from that in a standard chemical sulfite mill. Austenitic stainless steel (304 and 316) were selected for handling cooking liquor and have been performing satisfactorily for some time.

Groundwood Systems

Corrosion in pulp grinder stock solutions varies greatly depending upon type of wood being ground, water supply and which treating chemicals are added. Typical test results are given in Tables 7 and 8.[6] Pitting is severe and of the low weight-loss materials tested only 316 resists the conditions shown in Table 7. It should be noted that Tables 7 and 8 show solutions to be moderately corrosive to carbon steel and low alloy materials. Equipment of low corrosion tolerance should be made of the austenitic stainless steels. If iron discoloration of stock is a problem, consideration should be given to the use of 304 or 316 for other equipment handling stock solutions.

Bleaching Methods

After completion of the pulping proress, the final step consists of a bleaching operation to produce a pulp and resulting paper of the desired brightness. Chlorine, the most commonly used bleaching agent, is used in several different forms. Severe corrosion can be encountered in various bleaching operations as illustrated by Table 9.

These rates are typical of those encountered in hypochlorite bleaching. The only wholly suitable material tested is Hastelloy C. In more dilute solutions, 316, 317, Aloyco 20 and Monel are suitable.

Chlorine dioxide, one of the newer

forms of chlorine for bleaching purposes, poses some severe corrosion problems in its generation and use. Test results published by Teeple and Adams[7] indicate that Hastelloy C and Durichlor are the most resistant materials for handling higher strength solutions. Field reports indicate that Hastelloy C is not completely satisfactory under some conditions. Titanium is replacing Hastelloy C in some services. Reports indicate it is performing satisfactorily. In less aggressive solutions, complex stainless steels of the 20-type and molybdenum-bearing 316 and 317 materials are sometimes suitable. Non-metallic materials have been used satisfactorily under some conditions.

Concentrations of peroxide used in bleaching do not create major corrosion problems. If hydrogen peroxide is used as a source, care must be exercised in handling the undiluted (50 percent usually) solution. Spontaneous combustion will result if the material comes in contact with oxidizable organic materials. Spills should be immediately flushed away by generous use of water.

Aluminum is used for shipping peroxide and handling 50 percent strength solution. Austenitic stainless steels 304 and 316 serve very well for pumps and valves for 50 percent strength solutions.

Types 304, 316 and Monel have been used satisfactorily to eliminate discoloration from processing in steel equipment.

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Technical Topics Scheduled for July

Fluorocarbon Resin Piston Rings and Overbraided Hose Give Good Service, by L. A. Ferris

Gas Company Uses Cathodic Protection Training Program to Improve Installation Operations, by Cecil Gibson

Corrosion Problems of Central Power Station Turbines and Condensers, by A. Bayard Sisson

High Temperature Corrosion of Aluminum-Plutonium and Aluminum-Silicon-Plutonium Alloys, by H. C. Bowen

High Temperature Aqueous Corrosion of Aluminum-Uranium and Aluminum-Silicon-Uranium Alloys, by H. C. Bowen and R. L. Dillon

Laboratory Tests for Rapid Evaluation of Ship Bottom Coatings, by J. R. Brown

Pulp Digester Corrosion Control

Abstract

Calcium sulfate scale deposited on spot-welded stainless steel sulfite digester linings is believed to be the cause of pitting (from concentration cell effect) and stress corrosion cracking of the liner experienced at the British Columbia plant of Columbia Cellulose. The chloride concentration expected in the scale was not found in analysis. A 1955 test showed high chloride concentration in both the cooking acid and blow liquor.

Some theories are outlined about reasons for the corrosion damage observed in the digester, and repair procedure is described. Because of difficulty with Hastelloy welding rods, Ni-O-Nel was adopted for all welding in both the shell and vapor phase areas.

Lack of trouble with a clad digester is attributed to improved plant operations and some improvements in scale removing procedures. Better design of collector rings and pipe nozzles could eliminate many crevices in which scale forms, the author believes. Stainless steel for sulfite service should contain a minimum of 2.75 percent molybdenum and maximum 0.05 percent carbon. All surfaces should be ground to a high luster finish and fully protected during manufacture.   7.6.6
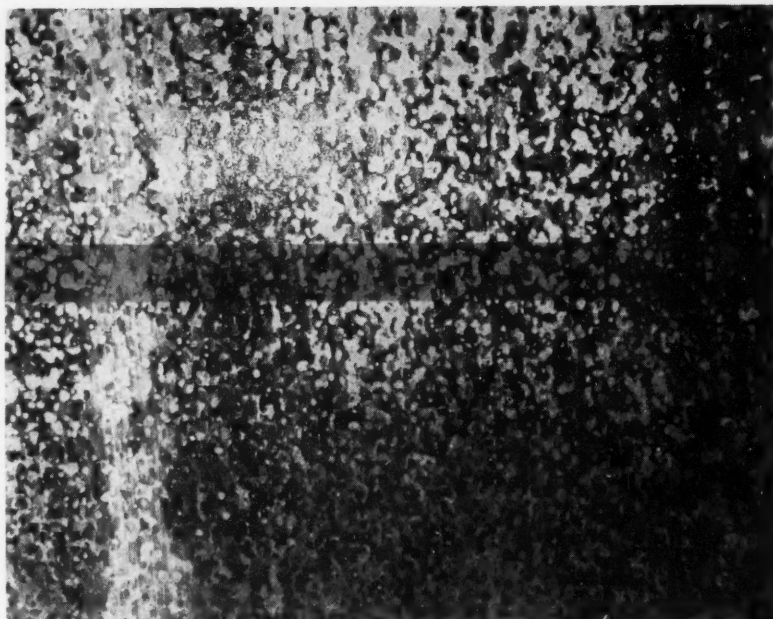
Figure 1—Scale on stainless liner of a digester.

Introduction

THE DIGESTER is said to be the heart of the pulp mill, and it may also be stated that the lining is the heart of the sulfite digester. Chips are introduced into the top of the vessel and five or six hours later pulp is blown or dumped out through the blow valve. Concurrent with this transformation, the lining of a digester must withstand temperatures of up to 150 C and pressures in excess of 100 psig.

The Columbia Cellulose Company has had a wide experience in digester linings. The spectacular failure of five brick-lined vessels soon after mill start up is well known in the industry. Changes made in the lining and shell design of these units, however, has since permitted a reasonably high level of production. In 1954, a sixth stainless steel lined digester was installed. This was the ninth unit of similar design to be put into operation in North America. The corrosion and corrosion prevention history of this spot welded liner is considered in detail in this article. A seventh stainless clad vessel was added to the sulfite mill in 1958.

Details of Process

In the sulfite process, digestion of wood is carried out at a high temperature in an aqueous solution which usually contains an alkaline-earth bisulfite and an excess of sulfur dioxide. In a mill which uses limestone as its base, the cooking acid is calcium bisulfite.

The acid is manufactured by melting and burning elemental sulfur to form the SO_2 gas. The gas is then cooled rapidly and passed upwards through limestone towers to unite with the calcium and form calcium bisulfite. The raw acid is composed of about 1 to 1.2 percent "combine" or sulfur dioxide combined with calcium and the remainder (some 5 to 6 percent) exists as free sulfur dioxide. Despite the most elaborate precautions, there will be traces of sulfur trioxide in the cooled gas and in the raw acid. At some point in the process, some of the sulfur trioxide picks up another oxygen atom and unites with calcium to form calcium sulfate. Calcium sulfate is the chief component of the insoluble scale which is the principal cause of corrosion in most sulfite digester linings.

While there is no full history of digester scaling, there are a number of known facts and many surmises. The scale is grey to black in color, insoluble in most acids and extremely hard. In digester circulating piping, this scale has been known to occupy as much as three quarters of the cross sectional area of a 10-inch diameter pipe and to defy all mechanical means of removal short of jackhammering.

A recent scale analysis made by the laboratory at Columbia Cellulose is given in Table 1. The procedure for this determination has been published.[1]

The most interesting facet of this analysis was the absence of chloride ion. In a mill which uses salt water-borne wood, chlorides generally are an accepted fact, and their volume is dependent on length of log storage in the salt water. In 1955, special tests conducted at Columbia showed a concentration of 0.032 percent NaCl in the cooking acid and 0.161 percent as NaCl in the blow liquor. A gain of 500 percent in chloride concentration could be attributed to wood chips.

Of the many reasons for scale deposit, there are perhaps three worthy of mention. Intermittent acid plant operation can cause inefficient or incomplete cooling of the burner gas and result in an excess of sulfur trioxide. High steam temperature creates local overheating of acid and subsequent escape of free sulfur dioxide. Lime also will be lost due to precipitation of the monosulfite. The sulfurous acid in the cooking liquor becomes oxidized to sulfuric acid by the air contained in the wood chips. The sulfuric acid reacts with the calcium to form calcium sulfate or gypsum, which precipitates out.

Details of Digester Structures

The sulfite digester is a pressure vessel some 60 feet tall and usually not more than 19 feet in diameter. Chips are dropped in through the top; cooking acid is pumped in at the bottom. The cooking liquor usually is drawn through strainers known as a collector ring located near the midline of the vessel. The liquor is re-cycled into the top and bottom of the digester by means of a circulating pump. Temperature wells, pressure and sample fittings, steam nozzles and relief inserts are placed strategically around the inner shell. For orientation, the digester can be said to have a lower cone, a cylinder, and top dome or head.

Until recent times, digester linings invariably were composed of acid resistant brick with lead sulfate joints and portland cement backing. Piping and valves were made from acid resistant bronze. Higher cooking temperatures and pressures necessitated double laid linings and stainless steel fittings. The discovery and popularity of soluble base acids such as ammonia and magnesium introduced the furfural membranes and the first stainless steel linings.

At Port Edward, experience with stainless linings has been confined to one

TABLE 1—Typical Analysis of Calcium Sulphate Scale

	Percent
Calcium	25.54
	25.31
Chloride	nil
Sulphate	51.70
	51.00
SO_2	7.55
	8.03
H_2O	1.2

NOTE: 5 percent of the scale did not dissolve in the ethylenediamine tetra-acetic acid but was later dissolved in aqua regia. An estimated 3 percent of the residue was found to be iron.

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Calcium Sulfate Scale Causes

Corrosion of Stainless Steel Pulp Digesters*

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spot welded and to one clad vessel. The former is a spot welded digester of Canadian manufacture assembled at Burrard Drydock in Vancouver and erected at the mill in one piece. It is 60 feet face to face and has an inside diameter of 17 feet, 9 inches. The lining, 0.109-inch thick, was factory spot welded on 1½ inch centers. The cone and cylinder liner plate are Type 316 ELC; the dome is Hastelloy F. The metal analysis is noted in Table 2.

A special stainless steel wear strip 1½ inches wide was welded to the liner at the two points of contact between the lining and the collector ring frames. The frames are supported on alloy[1] blocks which are welded to a ground overlay alloy pass on the mild steel shell. Thus the liner is not stressed by the weight of the collector ring.

All Type 316L joints were welded with Type 310 + Mo (SW 168).* The Hastelloy butts were welded with Hastelloy F electrode (SW 276).*

This digester was field stress-relieved at a temperature of 975 ± 25 F. The first cook started in April 1954.

Basis for the choice of the second stainless steel lined digester has been

(1) Esco 4 5 L: C, 0.03 maximum; Mn, 1.50; Si, 1.50; P, 0.04, S, 0.04, Cr 18-21; Ni, 10-13 and Mo 2.9 average.
* Designations of A. O. Smith Corp., Milwaukee, Wis.

published.[3] Reasons for the selection are as valid now as they were when the paper was presented in April, 1957.

Slightly larger than the spot welded vessel, the new No. 7 is 61 feet, 3 inches face to face and 19 feet inside diameter. The lining is Type 317 ELC ground to a lustre finish and clad to A 212 - B - FQ mild steel. Alloy welding consists of a first layer of Type 310 + Mo followed by two layers of Type 317L. The top head is conical in shape in contrast to the more common hemispherical design.

As a direct result of previous experience with a stainless lining, several important precautions were taken in the construction of the No. 7 digester. The welding sequence included a full X-ray after mild steel passes and a complete

dye penetrant and X-ray check after alloy welding. Field stress relief was carried out by the Linde low temperature method. The digester was first cooked in June, 1953.

Types of Corrosion Found

In the opening paragraphs, an attempt was made to set the stage for discussing digester lining corrosion by giving a brief description of the acid preparation and the details of digester construction. Because scale plays a very important part, an understanding of scale formation and its distribution through the system is necessary before discussing the effects on the linings.

Figure 1 shows the scale build-up on a smooth stainless surface. Although this

TABLE 2—Analysis of Spot Welded Digester Lining Materials (%)

Type 316 ELC		Hastelloy F	
C	.03 max	Cr	21—23
Mn	2.00 max	Ni	44—47
P	0.03 max	Mo	5.5—7.5
S	0.03 max	Cb & Ta	1.75—2.5
Si	1.00 max	Ta	0.50 min
Cr	17.50 min	C	0.08 max
Ni	11.00—14.00	Mn	1.00—2.00
Mo	2.50—3.00	P	0.04 max
Cb	0.10 max	Si	1.0 max
Ti	0.02 max	W	1.0
		Co	2.50
		Cu	0.15
		S	0.03
		FE	balance

Figure 2—Heavy scale between the collector ring and lining of a digester.

Corrosion
From
Calcium Sulfate Scale

encrustation cannot be removed easily by chemical or mechanical means, it must be eliminated to safeguard the underlying metal. Scale formed on the body of the digester does not continue to grow in thickness, but appears to reach a maximum, then slough and reform. In pockets such as those between the collector ring and the lining (Figure 2), deposit becomes heavier and consequently more destructive.

Contact or Crevice Effect

Contact or crevice scale deposit produces spectacular and exceedingly damaging results. Contact and crevice corrosion are most often given as reasons for initial surface deterioration.

Localized attack may result from an oxygen concentration cell under the scale. When such a condition exists, the acid solution under the scale has a lower oxygen content than the acid solution outside the scale. The area of the stainless in contact with the oxygen-deficient solution becomes anodic in respect to the portion of the metal in contact with the oxygen-rich solution. A galvanic cell is thus formed and a pit develops.[3] Because scale keeps the corrosives such as sulfuric acid in intimate contact with the surface of the metal, the pit enlarges.

Stress Cracking Effect

In areas where scale cannot be removed readily, the pitting increases to a depth at which tension stresses multiplied by stress concentration factors produce trans-granular or stress cracking.[4] However, if the scale is removed before serious cracking has taken place, the digester cooking acid will not appreciably increase the size of the pit. The scaling conditions seen in Figures 1 and 2 were found four to five years ago in the spot-welded No. 6 digester. At that time the lower knuckle was fairly well pitted, and several precautionary patches were welded to the liner. The remainder of the circumference was left untouched. Pitting in the unpatched portion has not increased in area or depth.

TABLE 3—Comparison of Composition of Type 316 L

	Standard Composition Percent	Wear Strip Analysis Percent
Cr	16—18	17.52
Ni	10—14	13.85
Mo	2— 3	2.75
C	0.03 Max	0.032 Max

TABLE 4—Composition of Ni-O-Nel

Element	Percent
Ni	38 — 46
Cr	19.5—23.5
Mc	2.5— 3.5
Cu	1.5— 3.0
Al	0.20 max.
Mn	1.0 max.
Si	0.50 max.
C	0.05 max.
S	0.03 max.
Ti	0.6—1.2
FE	Balance

Figure 3—Pitting and stress corrosion cracking of a stainless steel Type 316L wear strip in a digester.

On the other hand, where the scale is allowed to remain, cracks progress through the alloy plate thickness and enable corrosive liquids to attack the base metal. The collector ring wear strip, initially of Type 316L, was designed to protect the liner in an area of excessive abrasion. Failure of this first wear strip (Figures 3 and 4) by pitting and stress corrosion cracking necessitated its removal and replacement with Hastelloy F.

An independent analysis was made on the Type 316L after removal from the vessel. A comparison between the corroded section and the standard composition is listed in Table 3, which shows molybdenum to be in the required region for Type 316L and the carbons to be slightly off specification.

Erosion Effect

In recent months there have been strange erosion type fissures appearing in the new Hastelloy F stripping. These are confined to the area immediately below the support blocks and are shiny and molten in appearance. An analysis showed a slightly higher carbon and satisfactory chromium, nickel and molybdenum content. No evidence of pitting or stress cracking is visible in these depressions. Hastelloy material used subsequently for patching has been of the vacuum melted heats which have a carbon content of 0.02 percent. So far, these have been unaffected by the new form of attack.

Intergranular Precipitation Effect

Use of Hastelloy F for the original vapor phase lining was prompted by unfavorable experience in other sulfite mills with Type 316. The increased chromium, nickel and molybdenum content of Hastelloy gives it better resistance to pitting corrosion. In at least two mills, however, there have been other problems connected with this material. At Port Edward, the plate used for upper dome or dollar section was sensitized before fabrication of the vessel. An austenitic stainless steel can be sensitized if exposed to a temperature of 900 to 1500 F. This causes the carbon to be concentrated with the chromium along the grain boundaries to form chromium carbide particles. The condition is known as intergranular carbide precipitation.[5]

This particular theory has had some opposition because intergranular attack

has been known to occur in metals of very high chromium or very low carbon. The original Hastelloy plate would meet the first requirement but could not qualify for the second.

Intergranular Cracking in Heat Affected Zones

In the spot welded digester, intergranular cracking has become prevalent in the heat affected zones of the weld seams and to a lesser degree in the plate itself. Because these parts of the vessel were not severely scaled, the cracks became evident early in the life of the digester. Plate affected in this manner presents a challenge to those responsible for inspecting and maintaining the structure. First repairs made on the Hastelloy were simple weld overlays on top of the cracks.

These beads merely propogated more cracks. Patches applied over the liner only hastened the decay of the liner and permitted the admission of corrosive liquor to the mild steel plate beneath. Acid which finds its way under a liner of this type, preferentially attacks the weld nuggets. As these areas have been diluted by fusion with the mild steel as well and are under continual stress the attack is understandable. Very often, however, the cracks were filled with the calcium precipitate and no further corrosion took place.

Failure of a series of weld nuggets will cause a bulge in the liner and this can be seen by eye or found by thickness gauge readings.

Sequence of Repair Operations

The repair sequence is an interesting one and perhaps worthy of some consideration. It is a product of advice, trial and error but is not the final answer. Corroded metal can hold many surprises for the over confident.

That part of the lining which requires attention is removed by grinding and chipping. The underlying mild steel is cleaned thoroughly to remove all traces of deposited sulfides and repaired if necessary. The cleaning process is probably the most important part of the repair procedure. Corrosion products or spent liquors can crack weld repairs and necessitate further chipping and grinding before re-welding.

After the cleaning, a seal pass is laid

Corrosion
From
Calcium Sulfate Scale

(Continued From Page 16)

between the original liner and the mild steel. This will effectively separate the patched area from the sensitized metal. Individual 3-inch wide strips of Hastelloy plate are cut and welded to the mild steel. Three passes with ⅛-inch diameter electrodes are used to complete each joint. Each patch is drilled and tapped for a one-quarter inch pipe insert and tested with 80 psig of air. All welds are then checked for leaks with a soapy water solution. The result is a neat, independently tested liner section.

Finding suitable welding electrodes has proved to be a problem in the spot welded digester. Though the original Hastelloy rods were satisfactory, later shipments were unsuitable from a straight welding standpoint. Type 310 + Mo, the recommended electrode for welding mild steel, had a chemistry different from the parent Hastelloy plate.

At the same time, the 25-20 rod material produced numerous cracks when used in the dome section. Ni-O-Nel was first tested early in 1956 and later in that year was adopted for all dome repairs. It is now used for practically all work in the vessel, regardless of liner specification. Composition of this nickel-iron-chromium alloy is listed in Table 4.

Success of this weld metal is contrary to what is implied in the Schaeffler Constitution Diagram for stainless steel weld metals.[6] In his graph, Schaeffler compares nickel equivalent to chromium equivalent and classifies weld metal as austenite, ferrite or martensite. Ni-O-Nel with its high nickel-to-chromium ratio is strongly austenitic and should be more susceptible to cracking than Type 310. Columbia Cellulose experience may be a special case, however because the testing conditions were widely divergent. In any event, Ni-O-Nel has been used for over three years with no history of cracking.

Experience With Clad Digester

Now what of the experiences with the Clad No. 7 digester? From the troubled history of the spot welded vessel can it be assumed that the success of one and the failures of the other can be due entirely to their manufacture? Does the added molybdenum and the lustre finish of the Type 317 L provide absolute protection against pitting? Has the lower temperature stress relief sufficiently relieved the mild steel without damage to the stainless?

Most of these questions cannot be fully answered now. No repairs have been made to the newer vessel in its 19 months of operation. However, during the past two years there has been much less scale in the system and practically none evident inside the digesters. Number 7 went into operation with a double pipe water spray behind the collector ring and a portable shower that is designed to be placed in the top manway after each blow. Water at 20 C will remove scale by thermal shock. Steam chip packing, used to increase pulp tonnage, could have the added value of resulting in reduced oxygen in the chips.

Figure 4—Stress corrosion cracking of Type 316L wear stripping in a digester.

Inspection Methods Used

For inspection of stainless linings, the human eye cannot be overrated. No manufactured device can be as foolproof, as portable or as swift as the visual inspection. When the quality of persistence is added to sight, the combination is unbeatable.

Dye penetrants have gained considerable popularity in weld testing. On new construction they can often save time and money by indicating cracks before a weld is completed or has been X-rayed but in an operating sulfite digester, the sulfate scale usually plugs the cracks and prevents admission of the penetrant.

X-ray is at the same time the most costly weld testing method. Radiographs give a positive answer as to corrosion grooves or cracking and in the hands of a skilled technician often can indicate precise location of a flaw. The bulk and weight of the tube and the time required for exposures often limit this form of testing to small areas. In general, a digester cannot be held off the line for protracted periods to permit corrosion surveys.

Conclusions

As the experience reported in this article indicates, under the outlined conditions of operation, prevention of scale would eliminate a good deal of the corrosion. At Port Edward, scale has been reduced by improved acid plant operation, a desuperheater to lower steam temperatures and a system of cold water flushing.

Despite steps taken to prevent scale formation, it persists in crevices not adequately washed. Design of collector rings and pipe nozzles can be improved to eliminate many of small pockets and fissures in which scale collects and cannot be removed by thermal shock methods.

The choice of lining materials depends on economic considerations as well as corrosion aspects. Stainless steel for sulfite service should contain a minimum of 2.75 percent molybdenum and a maximum of 0.05 percent carbon. All stainless surfaces should be ground to a high finish and fully protected during manufacture.

Some More Recent Developments

Recent inspections of the new Lukens lined Type 317L vessel have revealed pitting in certain areas adjacent to several of the weld seams. This pitting has occurred where there had been excessive grinding, weld splatter or some such mechanical damage during construction of the digester. On the seams, pits have formed where the welding arc was started or broken. It can be concluded that Type 317L also is susceptible to a pitting attack in regions where the lustre finish has been damaged.

Vacuum melted Hastelloy F was used for wear stripping on the Lukens clad digester, and this has exhibited the same corrosion pattern as on the lined vessel. Ni-O-Nel electrode which showed to such good advantage earlier now shows surface roughening in the liquid phase of the digester. No such attack has been observed in the dome or vapor phase. Several Ni-O-Nel patches have been installed, and these will be carefully inspected during future shutdowns.

Acknowledgements

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Pulp Digester Corrosion Control

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Abstract

Success with hand weld overlays of Type 310 stainless to repair corrosion damage in bottom cones of Kraft digesters at Longview, Wash., induced Weyerhauser to use Type 310 stainless steel to repair complete digester shells of five units in 1956. Automatic welding guns were used with argon gas. At Everett, seven more digesters were overlaid in much the same manner. Type 316 was used for work at Everett because, by the time work was begun, some failures had been noted in the upper parts of the units at Longview.

Analysis showed that the original weld material was being diluted by the base metal in the ratio of 1 to 2.

In an effort to reduce the amount of dilution experienced, alterations were made in the method of deposit on the upper shell of the final unit at Everett. The gun was tilted 20 degrees to normal to effect greater impingement on preceding beads. Weight of deposit was increased, and rate of feed of argon gas also was increased to effect better shielding. The top four feet of the shell was given a double overlay. Tilting the gun did not materially improve the quality of the deposit. Double overlay produced a surface with an analysis close to that of the overlay wire.

Reports of inspections in several zones of the digesters are given. Significance of pits in overlaid material of this kind is emphasized.

Tests are being conducted using various types of weld overlay to find one more resistant. Some design changes were made in the digester. Impingement plates were installed to absorb erosive force of liquor and to provide cathodic protection to the overlay.

3.7.3, 9.6.6, 8.5.3, 6.2.5.

Figure 1—Hand overlay weld on No. 1 digester. West side of lower cone is shown, three feet from bottom, at 12 o'clock position.

Figure 2—Hand overlay weld of No. 1 digester. Southwest lower cone are three feet from bottom at 10:30 o'clock position.

Figure 3—Machine overlay weld on No. 1 digester. South side is shown, one foot up from junction of cone and wall at 9 o'clock position.

Corrosion Resistance
of
Stainless Steel Overlays
in
Kraft Digesters*

WEYERHAEUSER has been in the business of making Kraft pulp since the fall of 1948, when five carbon steel digesters were placed in service at its Longview, Washington, mill. Three more units were put into service in Springfield, Oregon in 1949 and six mild steel, carbon brick lined digesters started operating at Everett, Washington, in 1953. During this same period a number of Type 316 stainless steel clad units were installed.

First-hand experience has been with digesters at the Everett Kraft mill of Weyerhaeuser Company, and much of the history and data presented will concern these units.

Digesters at the Longview mill were fabricated of 1.625 inch A-70 firebox plate. In 1951 inspection of the bottom cone of one of these digesters revealed a localized reduction in shell thickness to one inch. This spot was overlaid

★ Revision of a paper titled "Weyerhaeuser's Experience With Kraft Digester Weld Overlay," presented at a meeting of Canadian Region, Western Division, National Association of Corrosion Engineers, Vancouver, B.C., February 10-12, 1960.

hand method using Type 310 stainless welding rod. This repair and subsequent repairs of a similar nature were inspected periodically and found in good condition.

This success and similar experience using Type 310 stainless, lime coated, 3/16-inch diameter hand rod led to the decision in 1956 to repair all digester shells of five units at Longview, using Type 310 stainless weldment overlay. The large area involved made it necessary to use an automatic shielded arc process.

Details of Overlay Procedure

Overlay was applied by an automatic welding gun supported on a variable speed travelling mount. Twenty-five pound level wound rolls of 1/16-inch diameter wire were used with argon gas containing 2 percent to 5 percent oxygen as the shielding agent. Oxygen in the gas improved flow characteristics of the overlay material and resulted in a smoother deposit than was attained with pure argon. Approximately 5 pounds of wire and 35 cubic feet of argon gas was

required for each square foot of overlay.

Three automatic units used in each digester operated at 25 to 29 volts, 300 amperes with a machine travel speed of 40 inches a minute. All units traveled on the same circular track, each covering a 120-degree arc on the shell with weld ending as a lap on the overlays deposited by the adjacent machine. At the end of each run, the arc was broken and the machine returned by hand to the original starting position. The unit was then indexed upward approximately 1/7-inch and the process repeated. When approximately 16 inches of shell had been covered in this manner, the staging and track were raised and the operation repeated. A crew of five men consisting of a foreman, three gun operators, and a relief operator was required. Because a considerable amount of electrical work and machine repair was involved in servicing, the operation required the full-time services of a plant electrician.

The five digesters were overlaid during an 8-month period between July, 1955, and February, 1956. As of Feb-
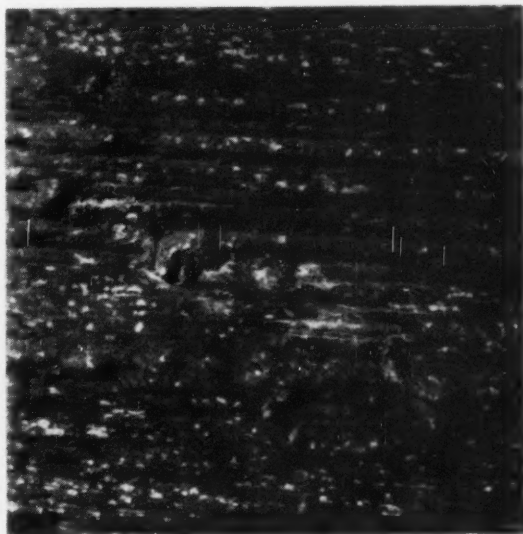
Figure 4—Weld overlay on No. 1 digester. Area shown is at 8 o'clock position, about 12 inches up the digester wall from junction of cone.
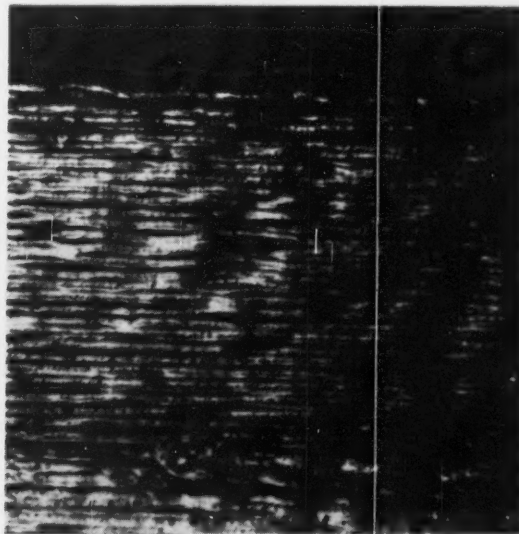
Figure 5—Weld overlay on No. 1 digester, six inches down from dome at 10:30 o'clock position.

Digester Overlays—

(Continued From Page 21)

ruary, 1960, condition of the overlays in the five digesters was as follows:

No. 1 repairs needed in upper 20 ft.
No. 2 "   "   "   " 15 "
No. 3 "   "   "   " 10 "
No. 4 "   "   "   " 12 "
No. 5 "   "   "   " 20 "

Repairs of Springfield and Everett Digesters

At Springfield, Oregon, three digesters have been repaired by the overlay method. No. 1 digester has had 236 sq. ft. covered; No. 2, 323 sq. ft.; and No. 3, 212 sq. ft. All repairs were made with Type 310 stainless using the shielded arc process. Because repairs were of a local nature and of necessity were made during short shutdowns, all overlay was manually applied with automatic welding guns. These repairs started in December, 1954, and were applied at intervals to July, 1957. All repairs were made in the lower areas of the digesters and are still sound.

At Everett, Washington, the six digesters as originally placed in service in 1953 were 1¼-inch A-285 grade "C" firebox steel protected by a 5-inch lining consisting of 2½ inches of carbon brick backed by 2½ inches of silica sand Portland cement grout. The aggressive nature of the cooking processes resulted in progressive failure of lining joint material.

In March, 1957, the decision was made to remove the carbon linings and overlay the digester shells with stainless steel weldment. All linings were removed and

cooking was carried on with liquors in direct contact with the mild steel shell until individual digesters could be removed from service for the overlay process. Because the wood supply for the Everett mill comes from salt water-stored logs, failure by corrosion had been experienced in digester filling and

Corrosion of Cladding

Some significant observations are presented here on stainless clad digesters of Weyerhaeuser Lumber Co. These concern five 10-percent clad digesters with one-inch thick shells at Longview. Cladding originally furnished in 1951 on these was Type 316, 0.095-inch thick.

Corrosion of cladding has taken place. This is most noticeable in same areas as severest corrosion which has been encountered in overlaid digesters.[1]

A series of metal thickness readings taken around the upper shell of one of these units is given in Table 3. Table 3 shows that up to 0.075-inch points of the original 0.095-inch of stainless steel have corroded away in the North position of the digester. Similar losses were found in other digesters.

Failure of the cladding has been observed at welded seams. These are not frequent enough to be alarming and are easily repaired.

Observations made on stainless-clad digesters tend to confirm the conclusions reached with respect to overlaid linings. These are (1) liquor impingement causes rapid corrosion and (2) non-uniformity of metal develops corrosion cells.

circulating piping before this time. Because of this serious corrosion problem and also because the digesters were not designed with a generous corrosion allowance, it was considered expedient to overlay the digesters as rapidly as possible. Also, the sooner the digesters could be overlaid, the better the surface would be for the weldment process.

Type 316 Selected for Overlay

By this time there was some evidence of failure in the Longview overlays. Because molybdenum-bearing stainless steels have proved most corrosion resistant in pulp mill service, the decision was made to overlay these units with Type 316 stainless material rather than the Type 310 used at Longview. Before making the overlay, each digester was sandblasted to bright metal and thoroughly washed with water to remove traces of blasting sand.

Overlay was applied in a manner similar to that described for the Longview digesters. The bottom four feet of the cones was overlaid with hand-held automatic guns. The remainder of the cone and the shell were overlaid automatically with the guns supported on variable speed traveling mounts. In all, about 1750 square feet per digester was overlaid.

Wire consumption varied from 6.5 lb sq ft on the first digester to 4.3 lb sq ft on the last. Argon consumption dropped from 32.0 to 20.0 cu. ft. per sq. ft. of overlay from first to last digester. With argon at 10 cents per cu. ft. and wire at approximately $1.80 per pound, these reductions were of considerable importance from the cost viewpoint.

During the process of overlaying one of the digesters, a blank was tack welded into one of the digester openings and was overlaid at the same time as the digester shell. This blank was removed later and cut up into samples so that the deposit could be inspected and analyzed. Total thickness of the overlay is 3/16-inch. A 4½ lb. sq. ft. deposit should give a ⅛-inch overlay, so it was obvious that the original stainless weld material was diluted by mild steel from the digester shell in the ratio of 1 part mild steel to 2 parts stainless steel. This was further established by laboratory analyses of the deposit from other sections of the same blank as shown in Table 1.

Before results of these analyses were known, it had been theorized that the overlay would be highly diluted at the interface but would resemble the overlay material very closely at the surface. The analyses, however, showed conclusively that dilution was uniform throughout. They showed also that the Ni, Cr and Mo contents had been reduced to two-thirds of original value, in the same ratio as the increase in deposit thickness from the ⅛-inch expected to the 3/16-inch obtained. This overlay was applied at 300 amperes. The uniform distribution of alloying elements in the deposit is to be expected. The deposit, because of this mixing, does not resemble the original Type 316 stainless steel.

By the time the last digester overlay was started, it was becoming evident at Longview that serious corrosion was developing in the upper portions of the Type 310 overlay. Upon advice of wire

lay process in progress on the Everett digesters were made. First, the gun was tilted downward 20 degrees so the arc would have more of a tendency to dig into the previous head and thereby reduce dilution. Approximately one-half of the shell was overlaid in this manner. Second, the weight of the deposit was increased from 4½ to 6½ lb sq ft, and argon volume was increased deliberately to insure adequate shielding. Third, the top four feet of the shell was re-overlaid with a deposit of 6.0 lb sq ft, making a total deposit of about 11 lb sq ft.

Four-inch diameter trepans later taken from each of these areas were sent to suppliers, several alterations in the over-

the wire manufacturers for analysis. Table 2 shows results of this analysis.

Analysis of the single overlay showed that tilting the gun 20 degrees did not result in a deposit significantly different from that obtained when gun was held normal to surface. Analysis did show that the double overlay was considerably richer in alloying elements, and the analysis more nearly resembled that of the original Type 316 wire.

Observations so far do not indicate that either of these deposits is substantially more resistant to corrosion than the overlay made by the original method.

TABLE 1—Analyses of Weld Deposit from Everett Digester

	C	Mn	P	S	Si	Ni	Cr	Mo
316 Wire	0.06	1.80	0.024	0.025	0.43	13.4	19.0	2.2
Weld Surface	0.124	1.34	0.626	0.020	0.20	9.19	12.94	1.48
Center	0.124	1.26	0.030	0.021	0.20	8.69	12.63	1.46
Interface	0.124	1.34	0.030	0.020	0.21	8.36	12.02	1.38

TABLE 2—Analyses Showing Difference Between Single and Double Overlay

	C	Mn	P	S	Si	Ni	Cr	Mo
Double Overlay Weld Surface	0.078	1.52	0.022	0.020	0.25	11.10	15.98	1.86
Interface	0.093	1.41	0.020	0.023	0.24	10.26	14.72	1.66
Single Overlay Weld Surface	0.091	1.30	0.021	0.021	0.20	8.76	12.84	1.38
Interface	0.087	1.30	0.020	0.020	0.19	8.64	12.58	1.38
Type 316	0.07	....	.....	.....	....	13.00	18.00	2.30

Digester Overlays—

(Continued From Page 23)

What Inspections Showed

Inspections indicate the following:

Cone Section

Most noticeable trouble is in spaces between weld beads where rust appears. Penetration behind these rust streaks has not been deep. Close inspection shows slight pitting and small vertical cracks across beads. No large amount of repair has been required.

Central Section

Same defects as in cone, but they appear to be considerably less serious.

Top 12 Feet of Shell

In areas of liquor impingement, corrosion is serious. Pits resembling tooth cavities have developed of sufficient depth to reach the mild steel shell.

Where poor weld beads occur, numerous cracks are appearing. In all areas of liquor impingement, weld appears bright and shiny indicating that the protective oxides are being continuously removed.

TABLE 3—Thickness Readings on Cladding in Inches

Ft. Down from Top Seam	POSITION IN DIGESTER							
	N	N E	E	S E	S	S W	W	N W
1.....................	.022	.080	.080	.080	.075	.055	.070	.022
2.....................	.022	.070	.075	.078	.075	.055	.070	.045
7.....................	.035	.075	.078	.078	.075	.060	.070	.055

Effects of corrosion are most serious in upper portion and tend to diminish toward the bottom.

Cavities which expose the mild steel shell are of particular concern because the shell will act as a sacrificial metal with the stainless overlay playing the noble metal role in the corrosion cell. Furthermore, the area relationship is extremely adverse. This will lead to rapid enlargement of cavities with resulting need for frequent inspection and repair.

Mild Steel Dome

No attack has been observed to date. This portion of the digester is not subject to liquor impingement or submergence, hence does not seem to corrode, indicating that vapors are not corrosive.

Corrective Measures

Each digester is inspected periodically. When defects are found, the cavity is drilled out or enlarged by using the arc-air process after which it is repaired with lime-coated Type 316 welding rod. On No. 2 digester, which was the first unit overlaid, 50 pounds of rod were required to make initial repairs. Five and one-half months later only 11 pounds were required.

Tests Seek to Locate Preferred Procedures

In an attempt to develop a repair procedure for later use in these digesters, a number of tests and experiments were conducted as follows:

1. A one square foot patch of Inco-Weld "A" was applied as an overlay over the original Type 316 deposit. Results were negative. After a two-month test, thick scale built up with corrosion taking place underneath. General surface attack was apparent also.

2. A one-foot square patch of Ni-O-Nel "65" was applied over original deposit. Results were negative. After eight months' exposure, metal was bright and shiny, same as adjacent Type 316 overlay. Cracks across beads were common.

3. Shower ring in recirculating line was modified to direct recycled liquor away from the digester shell. Installation has not been in service for a sufficient time to evaluate.

4. Two ¼-inch thick by 2 by 4-foot mild steel plates were installed adjacent to each other, spaced one inch from shell, to prevent direct impingement of liquor on shell. It was also reasoned that they would serve as cathodic protection for the overlay.

Results: Encouraging. Areas behind plates showed considerably less effects of corrosion than unprotected areas. Mild steel plate was noticeably corroded as expected. The top 6-feet of one digester is to be protected in this manner for more complete evaluation.*

5. Filming amines were sprayed into digester. Results: Negative. No apparent benefits could be observed.

6. Cathodic protection was investigated but considered impractical. Area of greatest corrosion could not be protected because the liquor level in digester drops during the cooking cycle.

Conclusions

Liquor impingement either during charging or recirculation is a major cause of digester corrosion.

The major cause of failure in weldment overlays is nonuniformity of the deposit. This nonuniformity results in corrosion cells which cause corrosion pits so evident in the failures. Extremely large noble metal areas provided by the stainless as compared to the small sacrificial areas within the pits cause rapid penetration of the pits.

If this mechanism is accepted as true, the type stainless used for overlay loses a great deal of its significance. Similar failures have been observed with Type 310 and 316; double overlay of 316 Inco weld "A" and Ni-O-Nel "65" over Type 316. Failure at welds in stainless-clad digesters further supports this contention.

In summary, results obtained from the overlay method of protecting Kraft digester shells is not completely satisfactory. However, a great deal of thought and attention have not revealed a better solution.

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* Subsequent to presentation of this article, the protective plates were installed. Inspection in December, 1960, revealed little or no attack behind the plates. Plates were replaced with no repairs needed.

Figure 1—Diagram of anode installation in pulp digester tank.

Pulp Digester Corrosion Control
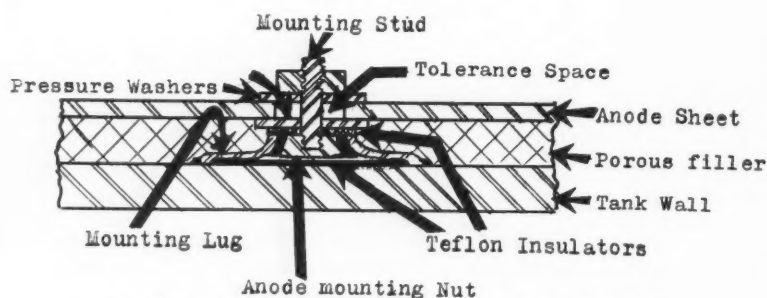
Figure 2—Insulated mounting lug for installing anode sheet on tank wall.
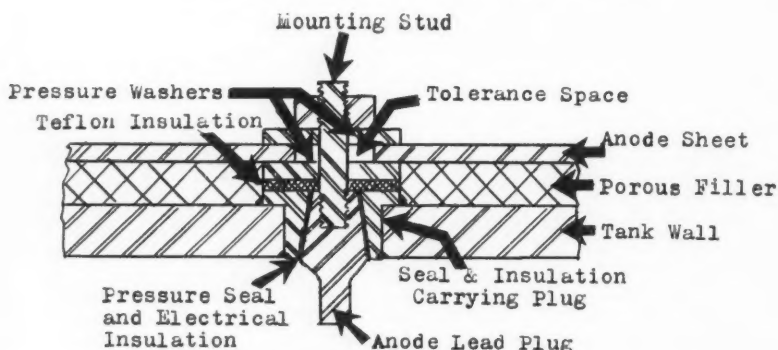
Figure 3—Anode lead insulating method and sealing plug.

Abstract

Proposes a system of cathodic protection for pulp digester tanks that will protect not only tank areas covered by liquid but also areas covered by vapor from liquid contents in tank. Outlines five requirements such a system should have. Describes inner lining of steel sheet used as anode with filler material between anode and tank wall. Filler suggested is cement and plaster of paris to achieve a porous material that will permit electrical conductance paths of moisture vapor through the material. Gives details of mounting anode sheets to tank and also a floating type platform for use inside tank to install and replace anode sheets. 5.2.1, 8.5.3

Introduction

CORROSION PREVENTION in pulp digesters is a recognized problem on which considerable time, effort and money is spent to minimize corrosion damage. This article proposes a solution to this corrosion problem with possible reduction in cost. This is not a report of an accomplishment but rather a proposed method of operation in which the most important phases have been proved. Combination of the proposals and the proved operation method provides a solution to the pulp digester corrosion problem which should prove to be successful.

Little of the work that has been done on cathodic protection of pulp digesters has been published. Companies operating cathodic protection systems on these

digesters generally believe that where it is possible to conduct cathodic current to the surface of the digester, corrosion has been eliminated from the tank wells. However, cathodic protection did not extend to the tank's area exposed to vapor, thus permitting corrosion damage to occur in that area.

Five requirements should be fulfilled by a cathodic protection system designed to prevent pulp digester corrosion:

1. System should protect the tank from the vapor phase and liquid phase of the contents.

2. Anode system should be electrically isolated from the tank. Because of the presence of high vapor content in the tank, current leakage usually occurs across insulation.

3. System must be able to withstand the forces developed inside the tank during loading, unloading and pressure fluctuations.

4. System must be simple and easy to install and to operate with ease of replacement when the anodes have been consumed.

5. System should provide means of determining the progress of corrosion on the tank without requiring dismantling of the cathodic protection system.

Proposed Method to Protect Digester Tank

The proposed method to protect the entire digester vessel and to fulfill the above five requirements makes use of the tendency of the vapor to create conduction paths for the protective current needed. This is done by applying a porous material to the entire tank

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Cathodic Protection Proposed for Vapor Area in Pulp Digesters*

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wall surface and applying a thin steel electrode over that porous material as shown in Figure 1 so that they conform to the tank's circumference.

With the inner steel layer as an anode, current can be conducted through the porous material along paths formed by adsorbed moisture which concentrates in the material. The tank wall then becomes the cathode of the system. This corresponds to the leakage conduction which is objectionable when it occurs at the wrong place. Because the porous material covers the cathode surface (tank walls), oxidizing and depolarizing materials are less likely to reach the cathode. Thus the tank walls will polarize effectively and remain so, even with small amounts of current flow per unit area.

Success of this proposed system depends on the method by which it is installed. Because all repairs or anode replacements must be made through the digester's manhole, no anode materials can be used that are wider than manhole's maximum diameter. Thus, the anode structure is a series of vertical strips mounted around the digester walls.

Figure 2 shows a method that can be used for mounting these strips to the tank wall and at the same time insulating the anodes from the tank. This mounting is composed of a circular steel

made to feed through a hole in the tank wall.

The inner flange can be welded around its periphery in a manner similar to that used for the mounting lug. Extension of the shank of this fitting can be welded on the outside of the tank if so desired for strength purposes. The anode lead plug comes through the center of this fitting with insulation from the anode plug fitting achieved by a glass frit which has been fired in place. This material forms an electrical insulation and a pressure seal. This method for insulation and sealing has been used in experimental installations with good success.

Number of anode leads passing through the tank wall will depend on the number of sections into which the cathodic protection system is divided. If all the anode plates can be bonded together by welding steel strip between them, then only one anode lead is needed. (See Figure 1.)

After the anode plates are installed, the filler material is installed by pumping a slurry made of a mixture of portland cement and plaster of paris. This is pumped through a hole in the anode plate, preferably at the bottom so that the slurry can be pumped upward to avoid air pockets. After the slurry is pumped, the opening in the anode is capped and the slurry allowed to set.

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lug which can be welded to the tank wall around the periphery of the lug. Mounted in the lug's center by a fired coating of glass is a nut used for securing the anode plate firmly to the wall. Over the top of this assembly is placed a fluorocarbon washer which is compressed between the mounting lug and the anode plate so that there is no electrical path from the mounting nut to the cathode.

Likewise, a fluorocarbon disc is inserted between the anode nut and the tank wall before the lug is mounted so no current leakage can occur in this direction. As a result, this portion of the anode circuit is protected from any anodic dissolution so that a new anode structure can be mounted when the old anode is consumed. The steel washers shown in Figure 2 both under and over the anode sheet are used to simplify fitting new anode sheets to the mounting lugs when replacement is necessary. The washer next to the mounting lug provides a close fit over the plastic washer for an effective seal. The washer over the outside of the anode sheet provides the necessary bearing to draw the sheet tightly against the mounting lug, even though the holes are not in perfect alignment.

These mounting lugs are installed at the center of each anode strip. One lug to every five to ten feet is considered sufficient to support the structures.

To apply a potential to the electrodes, insulated leads must be carried through the tank wall. A mechanism similar to the anode mountings can be used for this. Figure 3 shows a possible variation of this technique. The mounting is

No Watertight Seal Needed

The anode and porous systems are not intended to be a watertight seal to prevent vapor or liquid from contacting the tank walls. It probably would be better to construct this portion of the system for maximum porosity because success of the system depends on vapors collecting in the filler material to conduct current from the anode to the cathode.

Thus, no concern should be given cracks in the filler material. Function of this material is only as a spacer and a means of adsorbing vapors for electrical conduction. A cracked material will accomplish this as well as an intact structure. And the cracked material, being enclosed in a space from which it cannot escape, will sustain pressure applied to the anode by such actions as the chip filling or by pressure surges. Steady state operating conditions do not result in pressure differentials across the anode structure because of the porosity of the anode system.

Use of the filler material is the least proven of this proposed system. Use of portland cement and plaster of paris is suggested because of rapid setting and because dimensional change can be adjusted by proportioning the two powders. Assumed that it will leach out in time, the plaster will leave a network of cement structure which becomes more porous with time. This may be an advantage in offsetting any tendency for the corrosion products to block the current path through the porous material.

Porous Medium Not a New Idea

Use of a porous medium between the anode and cathode of a cathodic pro-

tection system is not a new idea. This proposed system is similar to underground systems above the water table level in which conduction is along the moisture path in what would otherwise be a relatively non-conducting medium. It seems reasonable to expect that the use of porous material between two plates will perform as satisfactorily as when two electrodes are buried in a porous material.

Corrosion on Process Side of Anode

A minimum of corrosion should occur on the side of the anode sheets exposed to the digester process. If the anode material is made more electropositive than normal, corrosion probably will be minimized on the process side of the anode because of the passivity which should develop.

Research has shown that there is a point of instability in the potential of steel in digester liquors such that if the potential starts out more electropositive than this point, the steel develops passivity. If the steel starts out more electronegative, it becomes active and corrodes.[1]

Suggested Platform for Changing Anodes

Time involved in building necessary platforms inside the digester tank for installing new anodes can be reduced by using a floating floor such as that

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Cathodic Protection—

(Continued From Page 27)

shown in Figure 4. This consists of a central structure lowered into the tank by block and tackle. Radial legs of the platform can be dropped in and mounted in place one at a time by engaging the pin attachment for each leg. Movable levers extending down from ends of the radial arms of the platform are operated from the center by a toggle arrangement suggested in Figure 4. These levers can be forced against the tank wall to provide platform stability while the central support absorbs the majority of the loading.

A platform can be mounted over the radial arms to cover the cross section area of the tank to make anode replacement simple and easy. When work is complete at one height in the tank, the radial lever arms can be loosened from the walls and the platform raised

or lowered, then locked in place and work continued with a minimum loss of time.

With this type supporting structure, anode installation and replacement is simple and quick. Anode sheets can be ordered pre-cut and pre-punched because tolerances in mounting would allow for inaccuracies in punching or in locating of the mounting lugs. The anode sheets could be thin enough and short enough for handling by hand in the tank.

Cost Estimates for Proposed System

Success of any proposal will depend on the economics. In figuring the expected service life of the anode structure, a current density of 50 microamps per square foot has been assumed. This value has been reported in TAPPI Corrosion Committee meetings as having prevented corrosion in liquid zones where the digester fluid and the mov-

ing pulp were in contact with the cathode and could depolarize it effectively. In this proposed system with the cathode separated from the digester fluid, the current possibly can be reduced to 10 to 20 percent of this amount.

Also, the assumption was made that there would be as much corrosion on the anode's process side as on the opposite side. This represents a conservative estimate for life of the anode material. From these estimates, it has been figured that ¼-inch thick anode sheet would last four years. The probability that holes would appear in the anode toward the end of its life would be of no major significance because the holes would make little difference in the protective action of the material remaining.

For a digester tank 10-feet in diameter by 40 feet high, the estimated cost of the anode sheet steel (at 8 cents per pound) would be about $1200. Es-

Figure 4—Diagram of adjustable work platform for installing and replacing anode sheet inside pulp digester tank. Arrow 1: stabilizing pressure point. Arrow 2: load support point. Arrow 3: pin attachment. Arrow 4: block and tackle support. Arrow 5: operating screw. Arrow 6: floor of platform. Arrow 7: tank wall.

timated cost to remove old anodes and to replace them should not be more than $5000, including labor and material costs. Estimates of man-hours required for this job indicate that the digester should be out of service about three or four days.

Based on the conservative life expectancy of four years for the anode system, annual anode cost would be about $1200. If a more probable life of eight to ten years is used, estimated cost would be reduced proportionally.

Estimated power costs, based on two cents per kilowatt-hour, would be about $35 per year.

Other costs involved would be for inspection to determine the extent of corrosion taking place on the tank walls. No satisfactory method has been established because the surfaces are covered —the outside with thermal insulation and the inside with the anode sheets and porous filler.

One approach might be a series of fixed inspection spots where holes could be made in the insulation for access to the tank's outside wall. After the gage measurements are made, the holes could be closed with a removable plug with equivalent thermal insulation as the original insulation.

Reference

1. W. A. Mueller. Corrosion Studies of Carbon Steel in Alkaline Pulping Liquors by Potential-Time and Polarization Curve Methods. I: Theory, Methods and Selected Results. *Can J Tech*, 34, 162-181 (1956).

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ANODE PROTECTED crab pot on left in above photograph is in good condition after seven weeks' exposure to salt water corrosion; the zinc anode (see arrow) has been virtually consumed in place of the wire mesh. Unprotected pot on right has been riddled with holes, making the pot unsuitable for trapping crabs.

Zinc Protects Crab Pots But Other Factors Are Unfavorable

Zinc anodes have been shown by field tests to be one effective method of preventing salt water corrosion on mesh wire enclosures used to trap crabs.

About a half million dollars of galvanized poultry wire goes into the construction of crab pots for the Chesapeake Bay area alone. These pots trap over 50 million pounds of blue crabs during the eight-month crabbing season running from April until late in November.

The pots, two-foot square devices made of 1½-inch wire mesh, have a lower chamber, which contains the bait holder, and an upper chamber. Crabs attracted by the bait enter through funnels in the lower chamber. When they lunge for the bait, their upward thrust carries them into the upper chamber, where they are trapped.

At the start of the season, the crab fishermen of Virginia and Maryland place about 200,000 baited pots in the bay. By August, salt water corrosion will have destroyed or made useless most of the original pots. Storms and mishandling will have taken their toll also. During the storms like Hurricane Hazel in 1954, crabbers sometimes lose over 50 percent of their traps. But corrosion causes the greatest loss.

Two Sets Needed Now

Until recently, three to four sets of pots were needed each season. But now, of the several brands of poultry wire available, one is more corrosion resistant, and crabbers say that only two sets are needed if made of this wire.

A new pot costs about $3, excluding labor costs as many crabbers make their own pots; the replacement pot costs about $1.70 if salvage parts (frame, weights, buoy) from the first pot are used.

Recognizing the corrosion problem facing crab fishermen, engineers of Federated Metals Division of American Smelting and Refining Company, 120 Broadway, New York 5, N. Y., several years ago tested small zinc anodes on several pots. The anodes are sacrificed to the salt water corrosion in place of the wire mesh. This experiment prompted the company to market a 1¾-pound anode for corrosion protection of crab pots.

Interest aroused by the use of anodes to protect crab pots led the American Zinc Institute and the Virginia Fisheries Laboratory to sponsor a study of anode protected and unprotected crab pots made of different wire grades and exposed to different salinities at several representative fishing sites. The Virginia Institute for Scientific Research, 2820 Grove Avenue, Richmond 31, Va., began the study in May, 1959.

To conduct the testing under actual conditions, the Institute had three commercial crabbers attach 1¾-pound anodes to new pots and set them at 3 to 30-foot depths in different sections of the York River, which empties into Chesapeake Bay. Pots were set at the river mouth where the average bottom salinity was 23 ppt (parts per thousand), 11 miles upriver where the average salinity was 20 ppt and 19 miles upriver where the average salinity was 16 ppt.

Test Pots Installed

At the mouth of the river, 15 anode protected and 5 unprotected pots made of the corrosion resistant wire (designated Brand A for test purposes) were placed on May 25. Average life of the unprotected pots was 20 weeks. At the end of the season, after 25 weeks of use, the protected pots showed no signs of deterioration. The anodes were reduced to pencil thickness.

Eleven miles upriver, 15 anode protected and several unprotected pots of Brand A wire were placed on May 25. One unprotected pot deteriorated in 15 weeks. At the end of the season, the protected pots were in good condition. Remnants of the anodes were larger than those on the pots farther downriver.

Nineteen miles upriver, on June 1, one anode was placed on a pot made of Brand A wire and 12 anodes were placed on some of the pots made of another wire (designated Brand B). Two unprotected Brand B pots lasted 9 weeks; the others a little longer. After 17 weeks the anodes had disappeared on all protected Brand B pots except one, and a second anode was attached to each pot. The anode on the Brand A pot was one-third its original size.

In all of the tests the zinc anodes proved effective in eliminating corrosion of the crab pots.

In discussing the findings, the report points out that, on a cost-of-material
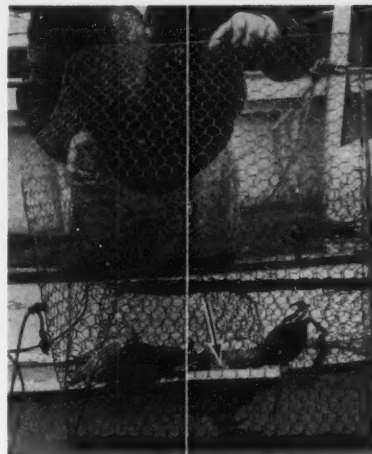
ZINC ANODE, indicated by arrow in photograph above, is used to protect crab pot constructed of galvanized poultry wire from salt water corrosion.

basis, the crabber would realize only a small saving the first year if he used anode protected pots made of the more corrosion resistant wire and paid as much as 80 cents for each zinc anode. Savings on labor costs would be significant if pots were purchased but less real if the crabber built his own pots. Worthwhile savings would accrue the second year if the usable life of crab pots were extended the first year by using a second anode.

Loss of Pots Factors

The report concludes that three factors hinder general acceptance of zinc anodes: (1) loss of pots by storms, strong bottom currents and mishandling, (2) availability of a more corrosion resistant netting and (3) relatively high cost of anodes.

The report recommends that characteristics of anode behavior should be determined for different environmental conditions so that modifications of quality and design might be made to improve anode efficiency and lower initial cost.

Zinc anodes used in the study were supplied by the Federated Metals Division of American Smelting and Refining Company. Each anode weighed approximately 1¾ pounds, was 7½ inches long and had a 1 by ⅞-inch cross section. Anodes were a high grade zinc with the iron content controlled to a maximum of 0.0014 percent.

About 15 feet of 18-gauge, 1½-inch hexagon netting, 2 feet wide, was used to construct each test pot. Surface area of the netting was estimated at 1000 to 1100 square inches.

COAL-TAR ENAMEL will protect a 60-inch steel water line being constructed to carry 75 million gallons of water daily for industrial purposes from the Smith Dam to Birmingham, Ala. The 35-mile water line will be completed this year.

Coal Tar Enamel Used to Protect Steel Water Line

Internal and external coal-tar enamel is being used to protect Birmingham's new steel water line. When completed this year, the 35-mile, 60-inch line will carry 75 million gallons of water each day from Smith Dam to Birmingham, Ala. A similarly protected water line's maintenance free service for 23 years and its good condition when inspected in 1960 were major factors in the Indus-trial Water Supply Board's decision to use coal-tar as protection.

Steel was chosen over rigid pipe materials because of terrain subsidence and high soil acidity.

Begun in 1960, the new line was made of locally produced steel pipe in 40-foot lengths, except for special sections, with wall thicknesses of $\frac{1}{2}$ to $\frac{11}{16}$-inch to compensate for pressure variations along the route.

At the fabricating plant, pipe lengths are lined, coated and wrapped. After the lengths are welded along the right-of-way and in the trench, joints also are field coated externally and internally. A fast drying primer is applied to cleaned sections, then the coal-tar enamel.

The primer is Bitumastic Jet-Set; the coal-tar enamel is Bitumastic 70B AWWA Enamel, produced by Koppers Company, Inc., Koppers Building, Pittsburgh 19, Pa.

Aluminum Used For Towers Reduces Painting Expense

An all-aluminum transmission tower line was built last year between Marcus Hook, Pa., and two New Jersey utilities. The line is 2.8 miles long. One side of the aluminum towers carries a double circuit 220 kv line; the other a new 132 kv line and an older kv line that had been carried on steel towers which were removed to make way for the aluminum towers.

Aluminum towers were used to reduce the expense and line outage time required for painting. The aluminum towers were economically competitive with steel when used in areas of industrial atmospheres, according to the builder of the towers, Philadelphia Electric Company.

Inventions Wanted By Defense Department

Future U.S. servicemen may wear a servo-assisted power suit, receive artillery support of shells with plastic components stronger than steel and use small firearms that are virtually noiseless, flashless and smokeless — if American civilian inventors can supply the necessary brainpower for development of these and 120 other new devices and design improvements requested by the Department of Defense.

The new developments needed by the Armed Forces are described in a free publication titled "Inventions Wanted" published by the National Inventors Council, Office of Technical Services, U.S. Department of Commerce, Washington 25, D. C.

New Australian Plant

A million dollar coated abrasive manufacturing plant will be constructed in Melbourne, Australia, by the Carborundum Company, Niagara Falls, N. Y. The new plant will be equipped with advanced facilities in the coated abrasive industry to meet the growing need in Australia and New Zealand.

Metal Fatigue 500 Miles Up

Investigation of surface effects on metals caused by the extreme of vacuum of space is included in $49,520 contract awarded by the Air Force to the National Research Corporation, 70 Memorial Dr., Cambridge 42, Mass.

Research will be concerned with the effects of fatigue on structural materials in the rarefied atmosphere encountered by satellites and space probes at orbiting altitudes beyond 500 miles.

Titanium Extrusion Study

A contract for development of a titanium extrusion process has been given to Republic Aviation Corporation by the Air Force. The contract covers advanced phases of study into new techniques for handling the high strength, difficult-to-shape metals needed in advanced aircraft and space vehicles.
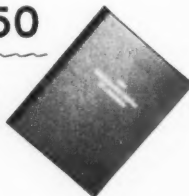
BOOK NEWS

Nondestructive Testing. by Warren J. McGonnagle. 455 pages, 6x9, cloth. 1961. The McGraw-Hill Book Company, Inc., 327 W. 41st St., New York 36, N. Y. Per copy, \$15.

A thoroughly illustrated (413) and extensively tabulated (65 tables) presentation of the whole field of nondestructive testing. Chapter headings: Introduction to test methods, verification, etc; visual testing, pressure and leak testing, liquid penetrant testing, thermal methods, X-ray radiography, gamma radiography;

Ultrasonics, dynamic testing, magnetic methods, electrical methods, eddy current methods, other methods, viz electrographic printing, sulfur printing, spectrochemical analysis, spark testing, etc.; thickness measurements.

Each chapter ends with a list of specific references. A combined subject and author index occupies 8 pages.

Annual Report to Congress, Atomic Energy Commission, 1960. 544 pages, 6 x 9¼ inches, paper. January, 1961. U. S. Government Printing Office, Washington, D. C. Availability not indicated.

A comprehensive summary of the year's activities of the AEC. Numerous tabulated data, lists of persons, committees, films and other useful information are included.

Slide Manual. W. R. Moran, chairman. 28 pages, 7 x 10 inches, paper. 1960. American Association of Petroleum Geologists, Inc., P. O. Box 979, Tulsa 1, Okla. Per copy \$1.25.

A comprehensive instruction book on the proper way to make and project slides illustrating talks. The three-color book is the work of a committee of AAPG that worked for two and a half years.

Contents include: Dimensions of original copy, legibility standards, testing legibility, use of typewritten copy, black and white vs color, preparation of colored slide copy, lettering on colored slides, ordering color transparencies;

Manufacture of slides, masks, thumb spots, binding, venting; types, testing; opaque projectors, overhead projectors, standard projectors, professional combination projectors; types and sizes of screens, dimensions, audience seating; types and use of pointers; AAPG visibility standards.

This illustrated book is replete with all kinds of information useful to those preparing slides. A comprehensive bibliography is included.

Metals Handbook. Properties and Selection of Metals. 8th Edition, Vol. 1. Taylor Lyman, editor. 1300 pages, 8¼ x 11 inches, cloth. 1961. American Society for Metals, Novelty, Ohio. Per copy \$30.

Reported to have two and one-half times as much information as was included in the 7th edition. Particular emphasis has been put on corrosion, consideration of which is included in almost every chapter to one degree or another. Also included are 12 major articles dealing with corrosion of metals and alloys. These articles cover 133 pages and contain 272 illustrations and 134 tables.

Of special importance is a 24-page article authored by the ASM Committee on Mild Steel Corrosion.

The contents include: Definitions and reference tables, carbon and low-alloy steels, cast irons, stainless and heat-resisting alloys, tool materials; magnetic, electrical and other special-purpose materials; aluminum and aluminum alloys, copper and copper alloys, lead and lead
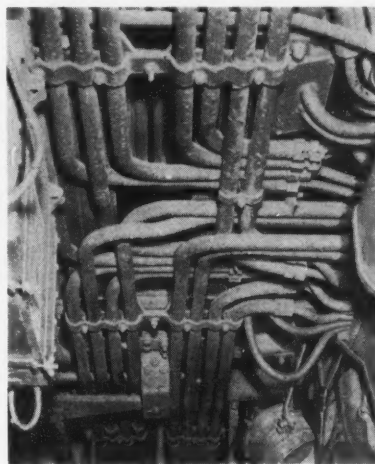
ALUMINUM CONDUIT has protected the electrical system of a commuter car of the Illinois Central Railroad since 1926. Recent inspection revealed the conduit ready for another 35 years' exposure to Chicago's corrosive atmosphere, weather and commuting service, according to its manufacturer, Aluminum Company of America, 1501 Alcoa Bldg., Pittsburgh 19, Pa.

alloys, magnesium and magnesium alloys.

Nickel and nickel alloys, tin and tin alloys, titanium and titanium alloys, zinc and zinc alloys, precious metals. Properties or pure metals are specially tabulated and there are reference tables of temperature and hardness conversions.

There is a 64-page alphabetical subject index. Each chapter ends with appropriate references to the data in the text. A total of 1300 metals specialists are named as contributors.

An Appraisal of Air Pollution in Minnesota. 73 pages 8½ x 11, paper, plastic bound. January, 1961. Minnesota Dept. of Health, Minneapolis. Copies available from Library, Robert A. Taft Engineering Center, Cincinnati, Ohio. Free.
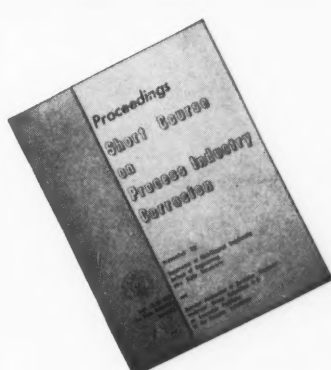
Another in the series of reports on studies of air pollution in various parts of the United States. This report covers a survey made in Minnesota during the interval October, 1959-July, 1960. There is a bibliography of 79 entries.

ASTM Research Program

An atmospheric corrosion research program covering 65 types of aluminum and zinc coated wire and wire products has been approved by ASTM Committee A-5 on Corrosion of Iron and Steel. Specimens will be exposed at seven sites in the summer of 1961.

Professional Engineers

The National Society of Professional Engineers will hold its 27th annual meeting July 4-7 at the Olympic Hotel in Seattle, Wash.

NEW DEVELOPMENTS IN ALLEGHENY STAINLESS STEEL CONDENSER TUBES MEAN

LOWER FIRST COSTS

BETTER HEAT TRANSFER

LONGER LIFE

CORROSION AND EROSION RESISTANCE

RESISTANCE TO IMPINGEMENT

HIGHER WATER VELOCITIES

In the last three years, over 3 million feet of stainless steel tubing has been installed in central station condensers throughout the United States. New developments, many sponsored by Allegheny Ludlum, have been responsible for this increase.

Automation, improved efficiency, and increased production have resulted in lower prices. Now stainless steel condenser tubes cost less than some of the copper alloy tubes. By actual price comparisons on some recent bids, Allegheny Type 304 Stainless Steel tubing was cheaper than a usual copper-base alloy in the same diameter. If high first costs have kept you from considering stainless steel condenser tubing with all their inherent advantages, it will pay you to re-investigate.

Increased operating data have shown that the in-use heat transfer rates on condenser tubes are much superior to the published data of a decade ago. Exhaustive tests made at a condenser completely re-tubed with Allegheny Type 304 Stainless Steel in May 1958 showed that the actual over-all heat rate on the turbine was improved over the 88-10-2 copper tubes previously used. Part of the answer is the thinner wall possible in the stainless tubing, 22-Bwg, compared with the 16-Bwg copper alloy tubing formerly used.

The superior strength of stainless allowed these thinner walls. In spite of the larger inside diameter, cooling water velocity through the tubes averaged ½ FPS more in stainless, although the pumping facilities were not changed. This increase in velocity, even though the ID is larger, is due to the lower flow resistance and improved interior cleanness.

In the condenser mentioned above, the utility and their consultant predict the life of stainless tubes as thirty years despite the highly corrosive river water involved where the pH may vary from three to six because of coal mine drainage. Previously, life for the copper base tubes formerly used was seven years. Re-tubing with stainless presents no problems, calls for no modification—it's as simple as re-tubing with copper.

Stainless tubes are much easier to clean than copper alloy tubes. They are harder and tougher. The mud and slime do not cling to the surface. With copper tubes, it was impossible to clean these condenser tubes without using oversize cleaning plugs which would have affected tube life. Practical cleanliness of copper tubing averages less than 60%. After re-tubing with Allegheny Stainless, one shot with nylon brushes restored cleanliness to the as-new condition.

Another major trend is the partial use of stainless tubes to resist excessive steam-side erosion. Many condensers are being specified or re-tubed with stainless tubes in the outer banks to resist blasting action or steam impingement. Generally, approximately 5% of the total tubes are specified stainless for the periphery. Even here, 22-Bwg stainless is usual where 18-Bwg or less is necessary in the copper alloys.
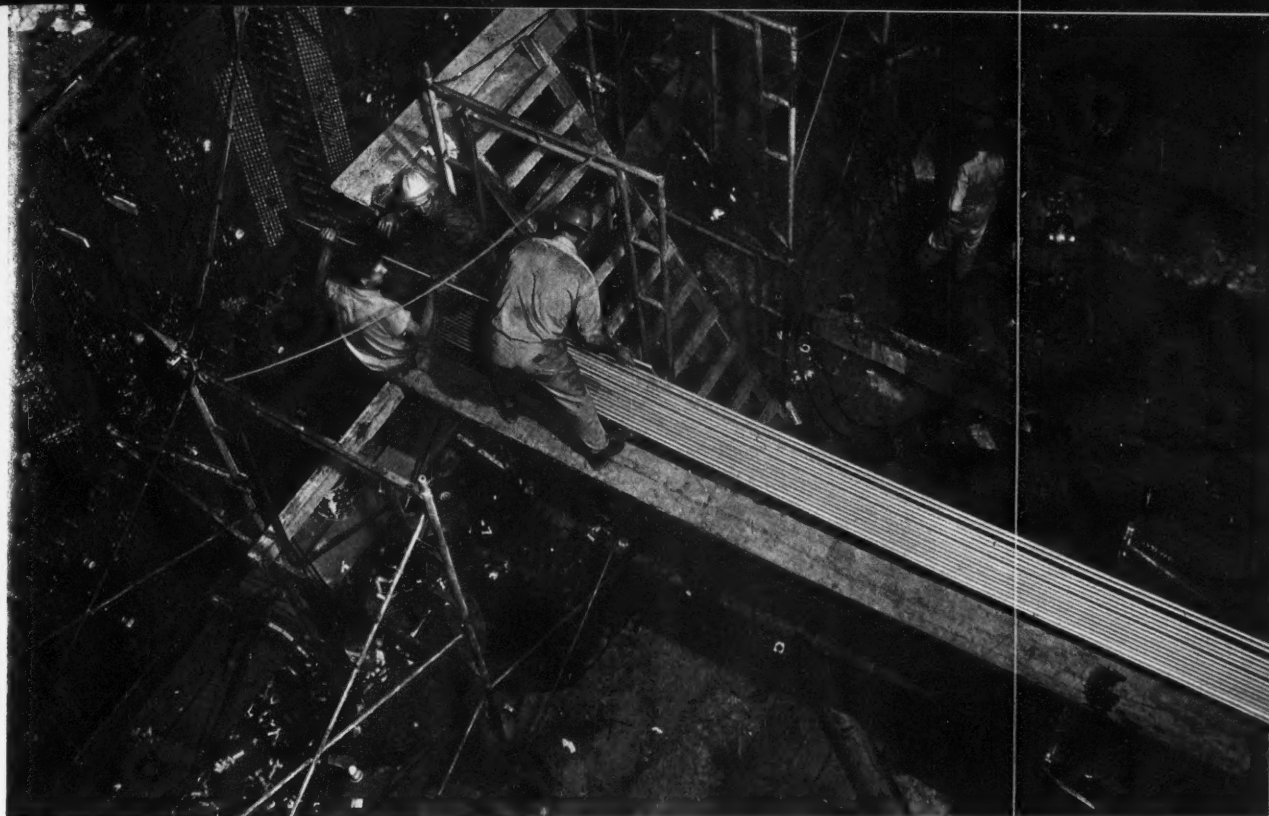
Retubing the air removal section of this condenser with Allegheny Stainless Tubes eliminated attack by the high ammonia content of the non-condensibles.

Another trend is the use of stainless in the air cooler or residual condenser section. Copper tubes tend to stress crack and fail because of the ammines used for water purification. Under these conditions, stainless tubes remain unaffected even under excessive build-up of ammonia in the non-condensibles.

On the horizons in heat transfer equipment design is an all stainless steel condenser that will result in an over-all size reduction. With the higher strength and the less resistance to water flow of stainless tubes, water velocity through the tubes can be doubled. Erosion and corrosion can be virtually eliminated. Right now, several consulting firms are evaluating this latest development.

Stainless steel condenser tubing is welded from high quality stainless steel strip on automatic machinery. After fabrication, they are cold drawn to increase strength and improve finish. Stainless steel condenser tubes are guaranteed against preferential corrosion attack at the weld. They can be rolled or welded into the tube sheet with the same equipment and procedures as with copper alloys. At the tube sheet, stainless steel resists oxygen release. There are no galvanic problems.

The trend to stainless steel condenser tubes is growing by leaps and bounds. For more facts, details, and general information, contact the nearest Allegheny Ludlum representative or write: *Allegheny Ludlum Steel Corporation, Oliver Building, Pittsburgh 22, Pa.*

No deterioration after 17 years of operating tests in river water made highly corrosive by coal mine drainage resulted in the selection of Type 304 Allegheny Stainless for the tubes in this condenser unit.

ALLEGHENY LUDLUM ⓐ AL

A-L products: stainless, high-temperature, electrical and tool steels; magnetic materials, and Carmet Carbides

2863

Gordon Research Conference Corrosion Program Dates Set

The Corrosion Program of the 1961 Gordon Research Conferences will be held July 24-28 at Colby Junior College, New London, N. H. The Physical Metallurgy Program will be held June 26-30 at Kimball Union Academy, Meriden, N. H.

The conferences, established to stimulate research and foster the informal exchange of ideas and cooperation among the participants, consist of lectures and group discussions.

The Corrosion Program is:

July 24: Corrosion Studies With the Field Ion Microscope, by E. Muller; Use of Contact Potential Measurements in Oxidation Studies, by A. Dravnieks; Electron Optical Studies of Thin Surface Films on Metals, by D. Pashley; and The Use of Elliptically Polarized Light in the Study of Oxide Film Growth on Metal Surfaces Immersed in Aqueous Solutions, by J. Kruger.

July 25: Nucleation and Growth of Oxide Films on Metals, by J. Benard; Oxide Nucleation and Growth on Magnesium, by T. Rhodin; Some Recent Results on Oxidation of Copper and Copper-Nickel Alloy Crystals, by A. T. Gwathmey; and Oxide Growth on Tin and Its Alloys, by W. Boggs.

July 26: The Oxidation of Metal-Carbon Alloys, by H. J. Engell; Some Problems in High Temperature Oxidation of Metals, by C. E. Birchenall; The Effects of Environment, Stress and Metal Structure on the Oxidation of Iron and Iron Alloys, by E. A. Gulbransen; and Formation and Reduction of Oxide Films on Iron Whisker Surfaces, by J. Laukonis.

July 27: Anodic Oxidation of Aluminum—Transient Effects and Oxide Structure, by M. Dignam; Anodic Oxidation of Lead in Sulphuric Acid, by R. A. Baker; and A Comparison Between Air-formed and Anodic Oxide Films on Iron, by M. Cohen.

July 28: Breakdown of Oxide Films and Pitting. General Discussion, by H. J. Engell.

The Physical Metallurgy Program is:

June 26: Field Emission Microscopy of Metal Crystal Nucleation From the Vapor, by K. L. Moazed; Substructures in Crystals Grown from the Melt, by C. Elbaum; Analysis of Substructure—Experiments and Theory, by S. Wiessmann; and Analysis of Defect Structures in Deformed Crystals, by C. N. J. Wagner.

June 27: Dislocation Distributions, Flow Stress and Hardening in F.C.C. Metals, by P. B. Hirsch; Special Arrangements of Dislocations in Deformed F.C.C. Metals, by U. F. Kocks; Dislocations and Substructures in Zinc Single Crystals, by V. V. Damiano; Short-Range Order, Point Defects and Dislocations in Alpha Brass, by L. M. Clarebrough; and Defect Structure in Dislocation-Free Crystals of Silicon and Germanium, by J. R. Patel.

June 28: Theory and Direct Observation of Antiphase Domain Boundaries and Dislocations in AB₃ Type Superlattices, by M. J. Marcinkowski; The Thermodynamic Basis of Morphological Development, by J. S. Kirkaldy; Electron Microscopic Observations on the Role of Dislocations in Precipitation, by V. A. Phillips; and The Role of Inter-facial Structure in Diffusional Transformations, by H. I. Aaronson.

June 29: Some Theoretical Aspects of the Formation of Proeutectoid Structures, by M. Hillert; The Isothermal Decomposition Products of Austenite, by W. L. Grube and S. R. Rouze; and Structures Produced by Diffusionless Transformations, by W. S. Owen.

June 30: Quantitative Electron Transmission Metallography, by J. E. Hilliard; Annealing Twins and Surface Topography, by M. J. Fraser; and Products of Transformations at High Pressure, by S. V. Radcliffe.

Additional information on the conferences can be obtained from W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, R. I.
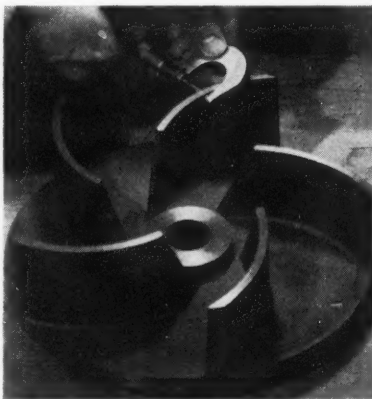
TITANIUM IMPELLER is first titanium casting made with a permanent mold by Titanium Metals Corporation of America. New permanent molds may reduce costs of cast titanium pump housings, valve bodies, fittings and pump sleeves.

Permanent Molds May Reduce Cost Of Titanium Castings

Small titanium castings such as pumps, valves and fittings are being mass produced with new permanent molds. The resulting reduction in cost of dies is expected to make titanium castings more competitive with other castings.

The cost of short lived graphite dies previously used made titanium castings impractical for most applications, according to the developer of the new molds, Titanium Metals Corporation of America, 233 Broadway, New York 7, N. Y. TMCA has made 40 castings with one new mold and believes 100 are probable; only 10 or 12, sometimes one, were possible with graphite dies.

The first commercial order of nine 12-pound impellers (see accompanying photograph) made with permanent molds proved that mold costs could be absorbed and shipments completed at prices lower than those charged for titanium welded assemblies now in use.

For chemical process applications where corrosion resistance is important, TMCA is casting unalloyed grades. Properties are similar to those achieved in bar products. Yield strengths ranging from 25,000 to 100,000 psi have been obtained in unalloyed cast products.

TMCA's present equipment limits mass production of titanium castings to those weighing 12 pounds with maximum size of 5 by 10 by 24 inches.

The new casting process, called Impel Casting, relies on the fluidity of titanium to produce high strength, intricate parts and requires a double melted titanium electrode with molten titanium forced into the die cavity. The shrinkage rate of titanium, 0.005 inch/inch makes timing a critical factor in feeding the metal into the die cavity and in pulling the cores. TMCA reports that 12-inch cores, about the size pulled from a cast automobile engine block, have been pulled successfully.

New Pentachlorophenol Wood Preserving Process

A new wood-preserving pressure process, trademarked Cellon, uses a liquefied gas in a pressure cylinder to deposit preservative chemicals in the fiber of the wood.

The Cellon-treated wood can be painted and is water repellent, free of raised grain, and unchanged in dimension. It has the properties and appearance of untreated wood, according to the manufacturer, Koppers Company, Inc.

To preserve wood against decay and insect attack, during the treating process, pentachlorophenol in the form of a dry crystalline salt is deposited in the wood. It is toxic to many wood-destroying organisms. As it is essentially non-soluble in water and has a low vapor pressure, the preservative cannot be leached and evaporates at a slow rate.

The process eliminates kiln drying because the wood is dry when removed from the cylinder.

The process is in the pilot plant stage. Commercial orders are not possible now, but samples are available from Koppers Company, Inc., Wood Preserving Division, 700 Koppers Building, Pittsburgh 19, Pa.

Hot Dip Galvanizers Elect New Officers

The American Hot Dip Galvanizers Association at its recent 26th Annual Meeting elected the following officers: President W. M. Boyles of Boyles Galvanizing and Plating Company, Hurst, Texas; First Vice President T. R. Gregory of Thomas Gregory Galvanizing Works, Maspeth, New York; Second Vice President Cooper Hawthorne of Metal Services, Inc., Port Neches, Texas.

Charles E. Perry was re-elected secretary-treasurer. John R. Daesen will serve as technical director.

The association is currently engaged in an awards campaign to develop new ideas in galvanizing technology and utilization. Ten awards of $1000 each are to be made. Additional information can be obtained from the association's headquarters, 5225 Manning Place N. W., Washington 16, D. C.

New Theory on Antiozonant Protection of Rubber

A new theory on how antiozonants protect rubber from ozone induced chemical decomposition has been advanced by members of Polymer Research and Development group of Bell Telephone Laboratories, 463 West Street, New York 14, N. Y. It is believed that radicals produced in a reaction between an amine antiozonant and peroxides created in rubber by ozone crosslink the surface of rubber, thus making it impervious to further ozone attack.

Antiozonants have been used for several years to prevent rubber degradation under field conditions, but the underlying mechanism of their protective action was not satisfactorily established. The new crosslinking theory may allow industrial technologists to extend the range and application of chemical antiozonants to inhibit environmental effects of ozone on materials.

Increasing amounts of smog in cities give rise to higher concentrations of ozone in the atmosphere, and means of protecting rubber from ozone chemical decomposition command the attention of more and more research scientists throughout the world.

Technetium Price Is Reduced

Price of technetium-99, a radioactive isotope which in extremely small amounts has shown promise in certain types of corrosion inhibitor studies, has been reduced to $100 per gram with a minimum charge of $10 for one-tenth a gram or less.

Previous prices ranged from $1600 to $2800 per gram, depending on amount

purchased. The isotope is available from Oak Ridge National Laboratory, Oak Ridge, Tenn., and is operated by Union Carbide Corporation for the Atomic Energy Commission.

Molecular Bonding of Stainless Clad Aluminum

Cladding aluminum sheet to stainless steel by molecular bonding results in a combination having the corrosion resistance, strength and luster of stainless steel and the thermal conductivity and corrosion resistance of lightweight aluminum, according to the manufacturer, Fairmont Aluminum Company, a subsidiary of Cerro Corporation, 300 Park Ave., New York 22, N. Y.

Tests by several cooking utensil manufacturers have shown that stainless clad aluminum has good metallurgical characteristics during fabricating operations, such as deep drawing, stamping, trimming, beading, spinning, arc welding, stud and spot welding, brazing, coining and surface finishing operations. Anticipated applications include automotive parts normally made of stainless, basic metal for rockets or missiles and liquid storage tanks.

Full-scale production is planned as soon as the current $10 million expansion and modernization program at Fairmont Aluminum plant at Fairmont, W. Va., is completed this year. The bonding process was developed by Composite Metals Products, Inc., of Washington, Pa.

Resin Storage Tanks End Metallic Pickup

Translucent storage tanks constructed of resin reinforced with fiberglass have replaced steel tanks formerly used to store a bonding solution at Owens Corning Fiberglas Corporation's plant at Aiken, S. C. In the steel tanks metallic pickup from corrosion was contaminating the bonding solution used to manufacture glass fiber mat.

The new plastic tanks are inert to the bonding solution and to external corrosion; they require little maintenance and no external painting. Also their translucent walls have eliminated dip-stick readings to determine the contents level. Previously, to take a dip-stick reading a cover had to be removed. Noxious fumes from the tank escaped, creating a personnel hazard.

The tanks, including the legs, are fabricated from resin produced by du Verre Incorporated, Box 37, Arcade, N. Y.
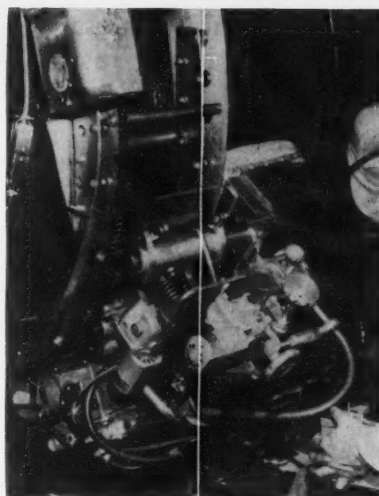
AUTOMATIC WELDING machine which encircles pipe can be adjusted to weld pipe of all sizes. The photograph shows 36-inch diameter pipe being welded in the field. Designed for welding stationary pipe under ordinary line-up conditions, the machine has been used with good results on a section of Pacific Gas and Electric Company's 296-mile portion of the Alberta-California natural gas pipeline. When further tests are completed and refinements made, the machine will be standardized and made available to the pipeline industry. Tests are being conducted under the direction of H. C. Price Company, Price Tower, Bartlesville, Okla., which developed the machine in conjunction with Crose-Perrault Equipment Company, Tulsa, Okla., and Hobart Brothers, Troy, Ohio.

European Corrosion Group Reviews Industrial Waters

The European Federation of Corrosion focused its 14th session on corrosion caused by industrial waters including raw, treated, recycled and waste waters. The meeting was held June 5 to 7 at Liege, Belgium.

Reports presented at the meeting are to be published and will be available from Cebedeau, 2, rue A. Stevart, Liege, Belgique.

Societies Affiliate

The 40,000-member American Society of Tool and Manufacturing Engineers has affiliated with the American Association for the Advancement of Science.

European Translations

A new cooperative effort between the United States and several European countries to provide broader distribution of translations of Russian and Eastern European scientific literature has been established.

A European Translation Center, sponsored by 12 member countries of the European Productivity Agency, has been established at the Technical University, Delft, Netherlands. The Office of Technical Services, U.S. Department of Commerce, is cooperating in this effort. Its publication, "Technical Translations," may be used as the circulation medium for the European Center's work.

Light Weight Stainless Hopper Car Being Tested

A new covered railroad hopper car with stainless steel interior will be tested in service carrying bulk materials ranging from chemicals to food products, according to its owner, United States Steel Corporation, 525 William Penn Place, Pittsburgh 30, Pa.

Protective linings are not needed, and the welded hoppers are free of traps where particles of one shipment might lodge to contaminate subsequent shipments.

The car weighs about 16 percent less than most steel hopper cars (58,500 vs. 70,000 pounds). With the recent development of a stainless steel called Tenelon, having almost twice the design strength of regular austenitic stainless steels, it was possible to use thinner gauge sheets of Tenelon to fabricate the car's hop-pers, cover, and other interior parts coming in contact with the lading.

USS Cor-Ten and Tri-Ten high-strength, low-alloy steels are used for the car's underframe, center sill and other bracing and support members. Regular air brakes are used.

Paint Society to Award Cash For Best Papers

For outstanding contributions to the technology and science of organic protective coatings, the Federation of Societies for Paint Technology offers a number of annual awards. Among these are the Roon Foundation Awards for the best original technical papers submitted for presentation at the Federation's annual meeting.

The Roon Awards consist of two classes. Open Competition Awards are open to anyone engaged in work or research related to the protective coatings industries including coatings manufacturers, raw material suppliers, research laboratories and universities. Class A Members Awards are limited to Class A members of the Federation. Each class offers a first prize of $450, a second prize of $250 and a third prize of $175.

Complete entry requirements for the Roon Awards can be obtained from the Federation of Societies for Paint Technology, 121 South Broad St., Philadelphia 7, Pa.

CAST STAINLESS MIXING blade prevents dough discoloration, speeds cleaning and increases bakery production at Bialy's, Inc., Flushing, N. Y. Stainless is immune to corrosive attack from organic salts and acids produced in the breakdown of sugar and starch and from the enzyme action of yeast. Carbon steel and cast iron blades, less resistant to corrosion, often discolored mixes or affected flavor.

Bakers Encounter Corrosion Too

New cast stainless blade has been specified for mixing dough to avoid discoloring the mix or introduction of metallic impurities that affect flavor. These problems, plus the need for frequent blade greasing, were encountered with mixing arms fabricated from carbon steel or cast iron.

Cast stainless is immune to corrosive attack from organic salts and acids produced in the breakdown of sugar and starch and from the enzyme action of yeast. Also the alloy is resistant to chemical cleaning, mechanical brushing and scouring. The mixing blade's surfaces are smooth and homogeneous with no crevices to harbor bacterial growth.

The blade, which produces a figure-8 mixing action, has speeded up mixing operations at Bialy's, Inc., Flushing, N. Y.

Designers at Peerless Bread Machinery Corporation, Sidney, Ohio, specified Alloy Casting Institute Type CF-16F alloy for the blade. Small amounts of selenium and phosphorous are added to improve chip characteristics. The alloy facilitates boring, grinding and facing operations.
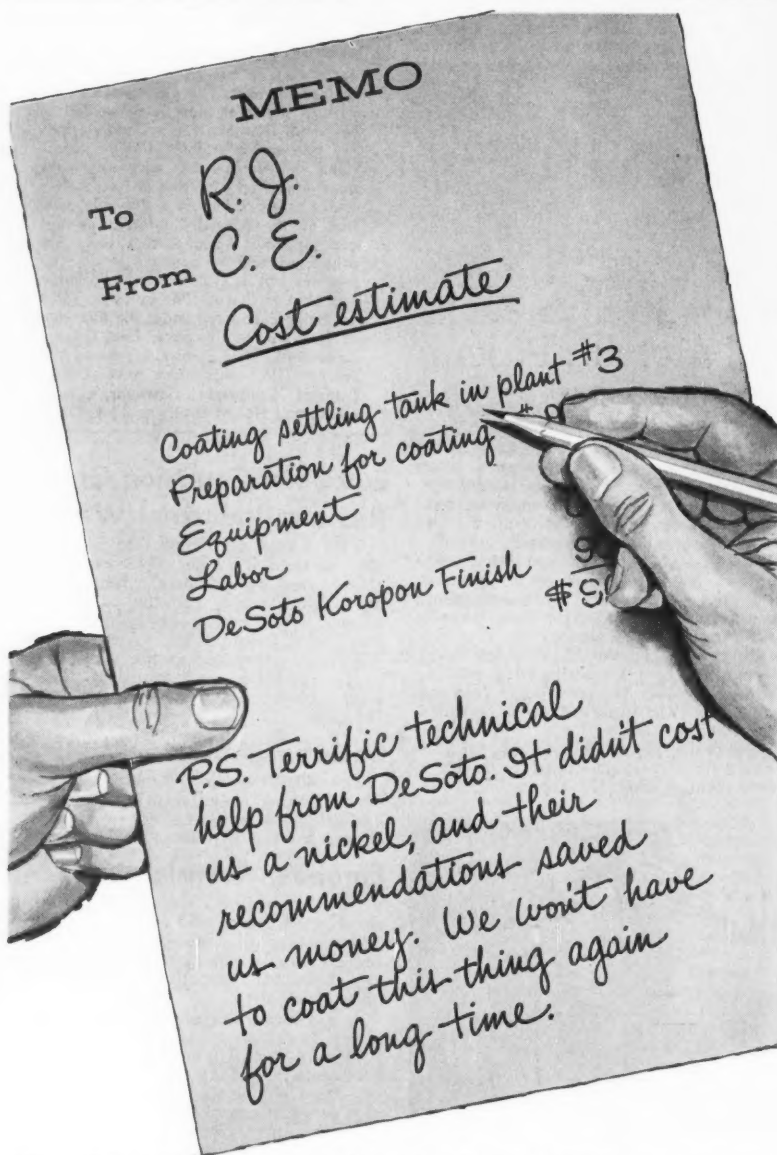
Grounding to Water Pipes Discussed as A-C Corrosion

Contradictory reports on corrosion of structures used as a part of the grounded neutral alternating current system in most homes caused San Diego Utilities Department to start a series of tests to get the facts. The utility suspected that several extreme cases of pipe corrosion were caused by alternating currents.

F. W. Waters, in his paper "Alternating Current Corrosion," prepared for presentation at the First International Congress on Metallic Corrosion held in London during April, outlines a series of experiments conducted to determine if the practice of grounding to water piping system does, in fact, cause corrosion.

He illustrates a situation in which a varying alternating current load is grounded to discontinuous piping systems. He also reports tests over a period of years in which the current flowing on water mains has been measured, the volume varying from fractions of an ampere to as much as an ampere.

Laboratory tests using coupons of iron, galvanized steel and copper subjected to alternating currents showed that the galvanized steel coupons lost about 1.72 grams when subjected to a flow of 1 ampere per square foot. Mr. Waters calculates the average loss to be about 4 percent of the loss that might be expected if the same coupons were subjected to an equivalent amount of direct current.

Among the other variables examined in the test series were the chemical content of the soils and water, the effects of a filtered circuit, an agar jel test which demonstrated clearly that alternating current does cause corrosion and others.

One of the collateral effects Mr. Waters sees in the present grounding practice is preferential corrosion of some underground systems favoring others in the circuit which are more noble in the electromotive series. Also considered was the effect of grounding both direct and alternating currents through piping systems as might occur in an industrial plant, and what effect the direct current might have in triggering bad effects from the alternating.

The utility is continuing its testing program.

Urethane Coatings Applied To Tank Cars For Testing

Field testing of a urethane coating on 26 railroad tank cars of Allied Chemical is being used to verify the coating's resistance to corrosive chemicals, abrasion and weathering.

Spilled chemicals may permanently stain paint and remove its gloss. Coatings on rail tank cars are attacked by grease splashes from wheels, strong caustic washing solutions, abrasive cinders and year-round exposure to weather. The use of a urethane system is expected to provide a tough coating which will keep the company's tank cars attractive longer than conventional coatings.

Test information can be obtained from Spencer Kellogg and Sons, Inc., Box 989, Buffalo 5, N. Y., manufacturer of urethane prepolymers. Allied Chemical's National Aniline Division, 40 Rector St., New York 6, N. Y.

REPUBLIC ELECTRUNITE *"DEKORON-COATED"* E.M.T. RESISTS SULPHUR DIOXIDE FUMES

In the sulphur dioxide atmosphere of the Anheuser-Busch, Inc., starch-making plant, all conduit is being replaced with "DEKORON-COATED" Electrical Metallic Tubing to cut maintenance and replacement problems in the electrical system.

Sulphur dioxide, a basic ingredient of the starch manufacturing process, eats away galvanized conduit in less than four months. "DEKORON-COATED" E.M.T. replacements have been in service up to twelve years under the same conditions and are still undamaged and serviceable.

Every length of "DEKORON-COATED" E.M.T. is coated with a tough polyethylene shield for highest resistance to fumes, gases, steam, and other corrosive materials. Couplings and fittings can be protected with plastic tape for full-length protection of the entire conduit system.

For complete information on corrosion-resistant "DEKORON-COATED" E.M.T., call your Republic representative or send the coupon below.

SULPHUR DIOXIDE ATMOSPHERE eats away I-beam in Anheuser-Busch starch plant, while "DEKORON-COATED" E.M.T. remains unharmed.

High Temperature Materials

The "Handbook of Thermophysical Properties of Solid Materials" is a compilation of published data on 12 major properties of solid materials that melt above 1000 F, including elements, alloys, ceramics, cermets, intermetallics, polymerics and composites. Commissioned by the U. S. Air Force for the specific use of government contractors in the missile, aircraft and nuclear science fields, the handbook comprises five volumes containing 4300 pages. It will be published in August but will be available in June at a pre-publication price of $75 from Macmillan Company, 60 Fifth Ave., New York 11, N. Y.

CELLULAR GLASS being applied to Melter-Washer Tower of new salt water conversion plant at St. Petersburg will insulate and protect the plant and piping. The freeze-type plant, designed to produce ice crystals which are pure water, is expected to furnish 35,000 gallons of fresh water daily.

Glass Foam Used To Protect, Insulate Salt Water Plant

A freeze-type salt water conversion plant at St. Petersburg, Fla., is coated with layers of high strength cellular glass for insulation and protection against corrosion. The incombustibility of cellular glass is an added safety factor, as the freeze process involves the use of combustible propane gas.

The glass insulation, unaffected by most acids and solvents and impervious to moisture, is Foamglas, a product of Pittsburgh Corning Corporation, One Gateway Center, Pittsburgh 22, Pa. Two layers were applied 2½ and 2 inches thick. Two coats of asphalt cutback reinforced with glass fabric formed the finish coat. All piping was insulated with 2-inch thick Foamglas pipe covering and the same exterior finish.

The plant is designed to produce ice crystals, which are pure water. Salt water and liquid butane are pumped into the tower. As the butane turns to a gas, pulling heat from the salt water, a slurry of ice crystals forms. Brine is then drained from the slurry. Next the ice crystals are washed clear of remaining salt water, melted and sent to storage tanks. Brine is dumped in Tampa Bay.

The plant, expected to produce 35,-000 gallons of fresh water a day at a cost of not more than fifty cents per 1000 gallons, will cost about $500,000. It is one of a series of saline conversion plants sponsored by the Office of Saline Water.

Adhesives

A prepared etching solution for making fluorocarbon polymers bondable to other materials has been introduced by Acton Laboratories, 1180 Raymond Blvd., Newark 2, N. J. Named Acton Fluoroetch Solution, it is in activated form of sodium in solution and reacts with fluorocarbon resin, extracting fluorine atoms at surface with formation of a carbonaceous film compatible with most adhesives. Technical bulletin describing properties and application is available from manufacturer.

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A cement-receptive film, factory applied to corrosion resistant polyvinyl chloride rigid sheeting, permits bonding to most substrates. Developed by Industrial Plastics Fabricators, Norwood, Mass., the epoxy adhesive is applied to substrate only; therefore corrosion requirements govern material cost rather than gauge requirements for structural strength. Developer uses process to fabricate its tube-axial fan line.

Coatings, Organic

A wood and concrete floor finish that provides durability and gloss two to three times longer than other varnishes is claimed by Du Pont Company, Wilmington 98, Del. Called Imron, the oil-free urethane clear finish is hard, fast drying, oil resistant with a high gloss. Used in textile industry for three years, Imron is recommended for wood floors subjected to heavy traffic. Bulletin is available from manufacturer.

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A line of heavy duty coatings packaged in color-coded, two-gallon kits containing equal mixtures of base and curing agent has been introduced as Farbo-Tile Coatings by Farboil Company, 801 Key Highway, Baltimore 30, Md. Based on epoxy and urethane resin formulations, kits are available for walls, floors, equipment, pools, maintenance and marine applications.

Desiccants

A dehydrating unit designed for complete and continuous moisture removal is being manufactured by Gas Drying, Inc., of Chatham, N. J. The unit, called a Dehyditrol, has a Rockwell-Nordstrom four-way lubricated plug valve and is self-contained for dehydrating compressed air and other compressed gases. Dehyditrols help provide greater accuracy in lab tests, increase flow efficiency, control corrosion and prevent hydrate formations, according to manufacturer. More information is available from Gas Drying, Inc., P. O. Box 56, Summit, N. J.

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Monsanto Chemical Company is marketing 105 percent phosphoric acid (45 percent more concentrated than 75 percent acid) from its new plant at Addyston, Ohio. Sold as Phospholeum, the concentrated acid is a natural dessiccant, renders inactive many common trace minerals such as calcium, aluminum and magnesium and is less corrosive than 75 and 85 percent acids, Monsanto states. Transported in tank car and truck quantities, it is easily handled at temperatures of normal usage and can be diluted to regular acid strength.

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Three new compressed air dryers of 40 capacities from 7.5 to 11,080 cfm at 100 psi are available. Dryers provide sterile, non-toxic, low dewpoint air to protect pneumatic equipment from corrosion, contamination and abrasion, to prolong life and accuracy of instruments and tools and to prevent freezing of exposed air lines. Operated without heat, power or regeneration, dryers require little maintenance and can be installed outside. Brochure is available from Van Products Company, 5763 Swanville Road, Erie, Pa.

Metals, Non-Ferrous

Lightweight, wear and corrosion resistant aluminum-silicon-copper extrusions for high production screw machine work are being produced by Ampco Metal, Inc., 1745 South 38th St., Milwaukee 1, Wis. The new alloy, Ampco-loy 405, is available in two extruded shapes—solid round and hexagon—for use as valve stems, valve seats, gears, marine hardware, pole line hardware, bushings, bearings and cams. The alloy is produced from virgin metals to closely controlled composition limits, is non-magnetic, will hot forge and is free machining.

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Commercial quantities of 99.9999 percent pure silver are being produced by Engelhard Industries, Inc., 113 Astor, Newark 2, N. J. Designated Grade E-4 or Spectropure silver, the metal is expected to be used in areas such as semiconductor manufacture and other electronics applications, metallurgy and catalysis in production of chemicals. It is produced in form of needles 1 to 3 mm maximum dimension, ingots 2 by 4 by 15 inches weighing 700 troy ounces and ingots 3 by 4 by 8 inches weighing 500 ounces. Ingots of other sizes, fabricated forms such as sheet or wire, and vacuum cast bars can be supplied.

Sealers

A non-fading, non-staining pure white base sealant called Thiocaulk for marble, limestone, brick, porcelain or cement surfaces is manufactured by Steelcote Mfg. Co., 3418 Gratiot St., St. Louis 3, Mo. With the stable white, colors to match surrounding surfaces can be made. Colors available are gray, black, aluminum pigmented, beige, limestone and brilliant white. Thiocaulk has properties of polysulfides. A paste when applied (with caulking gun, putty knife or trowel), it does not shrink, is water and chemical tight and lasts 20 to 25 years, according to Steelcote. This caulking is recommended for curtain wall construction, sealing thin wall porcelain, marble and masonry and for sealing joints in swimming pools.

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Bitumen rubber for curing in place by simple mixing and with adequate working time for pouring or applying is described in Bulletin 78 entitled Poly-Chem UT60 and UT60-F published by Dittbrenner Associates, Inc., 18 Oneida Ave. Rockaway, N. J. These caulking compounds are black elastomeric bitumen and vulcanize in place without shrinking to form elastic, soft rubber-like seals which contract and expand with joined surfaces of construction materials over wide temperature fluctuations.

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A seal using balanced hydraulic pressure to replace operational springs is being introduced by A. W. Chesterton Co., 6 Ashland St., Everett 49, Mass. Chesterton CounterPoise Seal (Type 500F) eliminates uneven peripheral spring forces, is free of vibration and provides a deep carbon face. Complete information is available from the manufacturer.

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Positive/Seal Klozure oil seals designed to resist extreme temperatures and claimed to be chemically inert and unaffected by corrosion have been developed by Garlock Inc., 602 N. 10th, Camden 1, N. J. In Garlock's lab tests, the new seals did not wear or score shafts, sealed at speeds to 3000 fpm. Seal includes steel case which positions component parts, gasket which holds sealing element and filled-Teflon sealing element which rides firmly against shaft.

Tapes

Fiberglas inner and outer underground pipe wraps for protection against outside pressures and corrosion are described in a new catalogue available from Fiberglas Sales to Manufacturers Division, Owens-Corning Fiberglas Corporation, Toledo 1, Ohio. Included are application techniques and guides to proper thicknesses, widths and laps. Dimensions, physical properties and other specifications of pipe-wrap products are listed.

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Adhesive asbestos tape for industrial assembly purposes is available from Johns-Manville. Called Besto-Tak, it can be used to 500 F in commercial grades and to 900 F in other grades. Available in thicknesses of 0.022, 1/32, 1/16 and 1/8 inches and in widths 3/8 to 6 inches. More information can be obtained from Johns-Manville's Packings & Textile Division, 22 East 40th St., New York 16, N. Y.

Valves

A high pressure shutoff valve with a Teflon seat compressed into a positive sealing "O" ring has been developed by Clayton Mark & Company, 1900 Dempster St., Evanston, Ill. When valve stem is screwed to closed position, portion of Teflon seat forms Teflon-to-metal seal. Type 18-8 stainless steel valve body is impervious to most fluids and is leakproof despite seat erosion or interference by foreign matter, according to manufacturer. Rated at 10,000 NSCWP and available in four sizes, ¼ to ¾ inch, valve is designed for easy opening and closing under high pressure.

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A stainless steel tubing valve designed for gas or liquid service at temperatures to 1000 F and at pressures to 30,000 psi is marketed as the AE Hi-Temp Valve by Autoclave Engineers, Inc., 2949 West 22nd St., Erie, Pa. Galling is eliminated because the two-piece stem does not rotate against seat.

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Compact, lightweight butterfly valves rated at 150 lb water pressure and covering pipe sizes from 2 to 18 inches are manufactured by Lunkenheimer Company, Cincinnati, Ohio. The valves have nickel plated cast iron or cast steel bodies with stainless steel trim and "O" ring seals to provide positive closure in vacuum or pressure service.

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A new ball valve designed for fast installation and disassembly for maintenance is produced by Clayton Mark & Company, Evanston, Ill. The valve, for controlling flow of liquid or gas in petroleum, chemical, food processing and other industrial piping systems, is available in stainless steel, carbon steel or brass in eight sizes, ¼ to 2 inches. An "O" ring prevents seal extrusion. The ball floats between seats, which seal regardless of direction of flow. Dual seats are available in Buna-N, Neoprene and Teflon and are interchangeable to meet most requirements. Maximum pressure rating for all sizes of valves with Buna-N and Neoprene seats is 300 psi. Teflon seats are rated to 600 psi for 1 to 2 inch valves and to 1,000 psi for ¼ to ¾ inch valves.

Welding

Tungsten Inert Gas Welding Guide to assist welders in proper use of tungsten electrodes has been published by Chemical and Metallurgical Division of Sylvania Electric Products Inc., a subsidiary of General Telephone & Electronics Corporation. Outlines welding procedures for aluminum, magnesium, stainless steel, deoxidized copper and titanium.

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Ultrasonic micro-joining, including heatless welding and fluxless soldering, with a new table-size unit is claimed by Cavitron Corporation, Long Island City, N. Y. The micro-joining kit welds leads 0.0001 inch diameter and consists of an ultrasonic transducer hand piece and four inserts. Although designed for research laboratories, the kit has been adapted to production problems. Inserts include attachment for tweezer welds, a ball-modification of tweezer insert, a spot welding insert and a vibrating table.

Miscellaneous

A modular periscope designed for remote observation where adverse conditions of heat, gas, pressure, radioactivity, etc., restrict visual access to the object under observation is manufactured by Kollmorgen Corporation, Northampton, Mass. The periscope can be assembled to one set of specifications, diassembled and reassembled for an entirely different use with a spanner wrench and a screw driver. It has an angular eyepiece telescope and viewing heads.

MEN in the NEWS

The Carborundum Company, Niagara Falls, N. Y., has promoted **John E. Niesse** to manager of its Process Development Department of the Research and Development Division.

NACE Member **B. J. Philibert** has been appointed industry manager at Baltimore, Md., for the Protective Coatings Division of Pittsburgh Chemical Company.

NACE Member **Herman S. Preiser** has been elected president and technical director of Chemionics Engineering Laboratories, One Bala Ave., Bala-Cynwyd, Pa.

Frederick L. Schuster has been named to the Board of Directors of Foster Wheeler Corporation, 666 Fifth Ave., New York 10, N. Y.

J. S. Smart, Jr., general sales manager of American Smelting and Refining Company, 120 Broadway, New York 5, N. Y., is 1961 president of the Metallurgical Society of AIME.

Arthur D. Little, Inc., Cambridge, Mass., has selected **Raymond Stevens** as president and chief executive officer during the absence of Lt. General James M. Gavin, recently appointed U. S. Ambassador to France. Four new vice presidents also were announced: **Albert E. Mignone** and **Richard S. Robinson,** of the Research and Development Division and **John F. Magee** and **Richard F. Messing,** of the Management Research Division.

Mahlon E. Wood has been appointed market development engineer for the American Zinc Institute, 60 East 42d, New York 17, N. Y.

The Awards Committee of the American Society of Lubrication Engineers has presented **W. A. Zisman** the 1961 ASLE National Award, the highest honor bestowed upon an individual by the society in recognition of an outstanding contribtuion to the field of lubrication. He is superintendent of the Chemistry Division of the Naval Research Laboratory, Washington, D. C.

R. G. Chambers has been promoted to senior sales representative at Jacksonville, Fla., for the Southeast-Gulf area of Pittsburgh Chemical Company's Protective Coatings Division.

NACE's 18th Annual Conference and 1962 Corrosion Show will be held at the Municipal Auditorium, Kansas City, Mo., March 19-23, 1962.

CORROSION ENGINEERING DIRECTORY

TECHNICAL COMMITTEE ACTIVITIES

Several Technical Committees Dropped At Buffalo Meeting

Termination of several technical unit committees and transferring of a group committee's activities to a unit committee was included among the business matters acted on at the March 15 meeting of the Technical Practices Committee held during the Buffalo Conference.

Acting on the recommendation of the Managing Committee, the Technical Practices Committee approved the change in scope for Unit Committee T-5D on Plastic Materials of Construction as follows: "To develop a master numbering system for the plastic materials of construction that are commonly used in the process industries and to publish data sheets showing physical, mechanical and chemical resistant properties.

The committee terminated T-6C on Protective Coatings for Resistance to Marine Corrosion and T-6E on Protective Coatings in Petroleum Production. It was recommended that the work of these two unit committees be merged with T-1G on Protective Coatings and Non-Metallic Materials for Oil Field Use.

Unit Committee T-6H on Glass Linings and Vitreous Enamels was terminated.

Group Committee T-9 on Marine Biological Deterioration was terminated and its work transferred to a new unit committee designated T-3J, which will have the same scope of activities as T-9 had. The unit committees of T-9 will become task groups of T-3J.

A task group was appointed to investigate proper placement of Group Committee T-7 (Corrosion Coordinating Committees). J. B. Prime, Jr., F. E. Kulman, Paul C. Hoy and T. J. Maitland were named to this group. Discussion was held on moving Committee T-7 outside the organizational structure of NACE Technical Committees.

Liaison between the API Division of Production Standardization Committees and NACE Technical Group Committee T-1 was approved. The chairman of T-1 will be the liaison representative.

Freedman

Roebuck

Corrosion Inhibitors Chairmen Elected

A. J. Freedman, project leader in cooling tower research for Nalco Chemical Company, Chicago, Ill., has been elected chairman of Technical Committee T-3A on Corrosion Inhibitors. An NACE member since 1954, he has a PhD in chemistry from New York University and worked for Standard Oil of Indiana before joining Nalco Chemical Company in 1959.

A. H. Roebuck, assistant manager of engineering and research with the Western Company, Midland, Texas, was elected vice chairman of T-3A. An NACE member since 1954, he has a PhD in chemistry from the University of Texas and formerly was associated with the Argonne National Laboratory at Lemont, Ill., and Continental Oil Company, Ponca City, Okla.

Industrial Painting Symposium Planned

Technical Committee T-6D on Industrial Maintenance Painting will sponsor its first symposium as part of the South Central Region Conference to be held October 24-26 in Houston. F. Parker Helms of Union Carbide Chemicals Co., Texas City, Texas, who is chairman of T-6D, will be chairman of the symposium.

The symposium will include two papers in the form of reports from two task groups: one on contract versus plant maintenance painting under chairmanship of Charles Fox of Sline Industrial Painters and another report on industrial maintenance painting engineering design, under chairmanship of John Weis of International Minerals & Chemicals Corporation.

Another feature of the symposium will be a coatings clinic conducted by Task Group T-6D-7 on Industrial Maintenance Painting Problems, headed by T-6D-7 Chairman Paul French.

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About $200 million was spent on classical phonograph records during 1959 in this country.

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Over a million new homes were purchased in 1959 by USA residents at a total cost of $18 billion.

Eight Discussions Held at Buffalo On High Temperatures

Eight 20-minute informal presentations were given during the March 15 meeting of Technical Unit Committee T-5B on High Temperature Corrosion. The meeting was held during the Buffalo Conference.

Moderators for the presentations were D. W. McDowell, Jr., and J. R. Myers, T-5B chairman and vice chairman respectively. List of the eight presentations is given below.

New Developments in Refractory Materials, by Roy Dial of Carborundum Co., Niagara Falls, N. Y.

High Temperature Probe, by David Roller of Magna Products, Inc., Anaheim, Cal.

McBee Punch Card System for Recording High Temperature Corrosion, Physical and Mechanical Property Data, by Miss Audrey Hunter of International Nickel Co., Inc., New York, N. Y.

High Temperature Corrosion in the Gas Turbine, by Allen Foster of General Electric Co., Schenectady, N. Y.

Corrosion Problems With High Nickel Alloys, by Doug Speed of International Nickel Co., Inc., Huntington, W. Va.

Education and Dissemination of Information on High Temperature Data, by Antone deS. Brasunas of American Society for Metals, Novelty Park, Ohio.

Magnetic Hydrodynamic Device, by W. E. Young of Westinghouse Electric Corporation, Pittsburgh, Pa.

New Developments for Handling the Fuel-Oil-Ash Corrosion Problem, by D. W. McDowell, Jr., of International Nickel Co., Inc., New York, N. Y.

T-5C Unit Meetings to Be Forums on Water Cooling

Technical Unit Committee T-5C on Corrosion by Cooling Water not only will act as a parent committee of several task groups organized in NACE regions but also will hold meetings. These meetings will be forums where manufacturers of materials of construction can meet people concerned with water treatment and owners of industrial systems.

Initially the committee will be concerned with problems associated with fresh water cooling.

W. A. Hess has been appointed pro tem chairman of T-5C. Additional information concerning the activation of T-5C can be obtained by writing him at Standard Oil Company of Ohio, Midland Bldg., Cleveland 15, Ohio.

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The 1961 South Central Region Conference and Exhibition will be held October 24-26 at the Shamrock-Hilton Hotel, Houston, Texas.

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The 1961 Northeast Region Conference will be held October 30-November 2 in New York City at the Hotel Statler.

NACE NEWS

Kansas City Conference Plans Are Under Way

Davidson

Gleekman

Goodnight

Grady

Moore

Rogers

Roller

Wright

Committee Chairmen Appointed to Make Local Arrangements

Plans are underway for the 1962 NACE Annual Conference to be held March 19-23 in Kansas City, Mo. General conference chairman Robert H. Goodnight of Cook Paint & Varnish Co., North Kansas City, Mo., has appointed his committee chairmen listed below.

L. W. Gleekman of Wyandotte Chemical Co., Wyandotte, Mich., is chairman of the technical program. His co-chairman is David Roller of Magna Products Co., Anaheim, Cal.

Conference co-chairman is Jack L. Grady of the J. L. Grady Company, Kansas City, Mo.

Other committee chairmen are O. E. Moore of Panhandle Eastern Pipe Line Co., entertainment and fellowship; Fred H. Rogers of Great Lakes Pipe Line Co., publicity; Forrest E. Davidson of Southwestern Bell Telephone Co., properties; and John E. Wright of Gas Service Co., local arrangements.

Mrs. Robert H. Goodnight and Mrs. Jack L. Grady will be in charge of the ladies program during the Kansas City conference.

Caldwell to Handle Liaison Work Between NACE, API

Liaison between standardization committees of the American Petroleum Institute and the NACE technical committees will be handled by J. A. Caldwell of Humble Oil & Refining Co., Houston, Texas. Mr. Caldwell was designated for this post by E. C. Greco, NACE president.

Mr. Caldwell, a member of the NACE board of directors representing South Central Region since 1959, has been active in association affairs since 1946. He

Caldwell

has held offices in the Houston Section and the South Central Region, and has been active in technical committee work. He was chairman of Technical Committee T-1D which is concerned with corrosion of oil field equipment.

He is senior research engineer, production research division, with his company, and is author and co-author

of several technical articles on corrosion control. He has an MS in Physics (1935) from Louisiana State University.

J. E. Ubben, assistant director of the Division of Production, American Petroleum Institute, has named Mr. Caldwell a member of four committees: on standardization of tubular goods; valves, fittings and flanges; of production equipment and corrosion fatigue testing.

L. L. Whiteneck Promoted By Port of Los Angeles

Lawrence L. Whiteneck, president of NACE for 1958-59, has been appointed chief harbor engineer of the Port of Los Angeles. He has been the municipal port's administrative engineer for the past two years.

Three Slide Shows Available

Three 35mm color slide shows are available free to NACE Sections and other interested groups for program use. The three slide sets, described below, are accompanied by scripts for oral comments as the slides are shown.

1. 17th Annual NACE Conference and 1961 Corrosion Show: 72 color slides showing main activities of conference plus close-up views of many booths at the Corrosion Show. Suggested as good survey of conference for persons who did not attend the Buffalo meeting. Program time: 30 to 45 minutes.

2. Surface Preparation by Sandblasting: 18 color slides showing various specifications of sandblasting for sur-

face preparation. Copies of technical paper by E. W. Oakes are sent with slide set. Specify number needed. Program time: 20 to 35 minutes.

3. 1960 Corrosion Show: 102 slides showing many of the booths and some of the products exhibited during the conference held last year in Dallas. Program time: 30 to 45 minutes.

Persons or groups interested in using the slide sets should send booking requests as far in advance as possible to Durwood Levy, NACE Central Office, 1061 M & M Bldg., Houston 2, Texas.

Slides can be shown on most standard slide projectors designed to handle 35mm color slides.

South Central Region

SYMPOSIA CHAIRMEN for the 1961 South Central Region Conference to be held October 24-26 in Houston are making final arrangements for the technical program. Seated from left to right, they are William G. Ashbaugh of Union Carbide Chemicals Co., chemical and process industries symposium; J. A. Caldwell of Humble Oil & Refining Co., oil and gas production symposium; M. A. Riordan of Rio Engineering Co., aluminum symposium and chairman of the technical program; Arthur C. Flory of Mavor-Kelly Company, properties chairman for the conference; L. G. Sharpe of Texas Eastern Transmission Corp., principles of testing and evaluation symposium; and Marion E. Frank of Tennessee Gas Pipeline Co., cathodic protection symposium. Not shown is Dan B. Stauffer, marine and offshore symposium.

Ten Symposia Scheduled For Oct. 24-26

Region Conference Program in Houston

Ten symposia are scheduled for the South Central Region Conference to be held October 24-26 at the Shamrock Hilton, Houston, Texas.

The symposia are given below with their scopes.

ALUMINUM—Metallurgical and corrosion characteristics and applications for marine, atmospheric, chemical, petro-chemical and pipelines will be discussed, including cathodic protection. Chairman is M. A. Riordan of Rio Engineering Company, Houston, Texas.

OIL AND GAS PRODUCTION—Principles and field practices concerned with corrosion reduction in well tubing, casing, wellhead fittings, flow lines, treaters and tanks will be covered. Chairman is J. A. Caldwell of Humble Oil & Refining Company, Houston, Texas.

UTILITIES—Experiences and practices of corrosion control in the gas, water and electric utilities will be included. Chairman is D. E. Simmons of Houston Lighting & Power Company, Houston, Texas.

INDUSTRIAL MAINTENANCE PAINTING—Interim reports of three or four task groups of NACE Technical Committee T-6D on Industrial Maintenance Painting will be given. A Coatings Clinic will be held by members of T-6D-7 to answer questions on industrial maintenance painting received in advance of the clinic and from the floor. Paul French of Humble Oil & Refining Company, Baytown, Texas, will moderate the clinic. F. Parker Helms of Union Carbide Chemicals Company, Texas City, Texas, is chairman of the symposium. (See additional story on page 49.)

CHEMICAL AND PROCESS INDUSTRIES—Several new metals and alloys, their methods of manufacture and fabrication, mechanical properties and corrosion resistance will be discussed. The metals and alloys are ductile iron, precipitation hardening stainless steels, and titanium-zirconium-tantalum and lead bonded steel. Chairman is William G. Ashbaugh of Union Carbide Chemicals Company, Texas City, Texas.

PIPELINES—New materials and procedures will be discussed with emphasis on uses of aluminum pipe and results. Internal cleaning procedures for pipelines also will be given. Chairman is A. T. Surber of Trunkline Gas Company, Houston, Texas.

MARINE AND OFFSHORE—New corrosion controls will be covered for use on offshore oil and gas facilities and marine structures. Chairman is Dan B. Stauffer of Humble Oil & Refining Company, Houston, Texas.

CATHODIC PROTECTION—Field applications of cathodic protection to structures and underground installed plant and equipment will be presented. Chairman is Marion E. Frank of Tennessee Gas Pipeline Company, Houston, Texas.

GALVANIC ANODES—Aluminum, magnesium and zinc anodes and their uses, limitations and alloying ingredients will be covered by papers from manufacturers. There will be a round-table discussion by users of these anodes on installations and experiences. Chairman is Walter P. Noser of Humble Pipe Line Company, Houston, Texas.

PRINCIPLES OF TESTING AND EVALUATING—To be covered are (1) fundamentals of evaluation testing, including design of lab and field programs and their correlation, (2) principles of evaluating corrosion problems and designing protection and (3) principles of testing and evaluating metals, coatings, inhibitors and operation changes. L. G.

Sharpe of Texas Eastern Transmission Corporation, Houston, Texas, is chairman.

Exhibition to Be Held

The 4th South Central Region Exhibition will be held concurrently with the conference at the Shamrock Hilton. Floor plan of the exhibition was given on Page 54 of the May issue of CORROSION. Booth space can be reserved by contacting NACE Exhibits Manager R. W. Huff, Jr., 1061 M & M Bldg., Houston 2, Texas.

C. L. Woody Heads Committee Chairmen For Houston Meeting

Charles L. Woody of United Gas Corporation, Houston, is general chairman of the South Central Region Conference to be held in Houston October 24-26. Ben Russell of Russell & Sharpe, Inc., is vice chairman.

Other committee chairmen are Local Arrangements—J. E. Rench of Napko Corporation, Technical Program—M. A. Riordan of Rio Engineering Company, Finance—R. A. Brannon of Humble Pipe Line Company, and Publicity—Rudy Zorn of Cameron Iron Works, Inc.

Brannon

Riordan

Rench

Russell

Woody

SHREVEPORT SECTION presented a plaque for leadership and service to 1960 Chairman Bob Naremore (center) of Sunray Mid-Continent Oil Company. New section officers presenting the plaque are (left to right) Vice Chairman O. A. Tefankjian of Texas Eastern Transmission Corporation, Chairman Grady Howell of Tube-Kote, Inc., Trustee M. J. Olive of Corrosion Control Associates and Treasurer Gene Moore of Tretolite Company.

South Central Region

Complete Program Given For Teche Short Course

Complete program for the June 7-8 Teche Section Short Course is given below. The course will be held on the campus of Southwestern Louisiana Institute at Lafayette. Registration fee will be $20 including lunch for both days of the course, the social hour and a banquet on June 7.

The course is designed to be of interest not only to corrosion engineers and technical personnel but also to field foremen, field engineers and other persons not working directly in corrosion control. Particular attention is given to problems encountered in the Gulf Coast area.

Wednesday, June 7

Introduction and welcome by R. L. Davis, short course director, John Smith, Teche Section chairman, and G. G. Varvaro, Department of Petroleum Engineering, Southwestern Louisiana Institute.

"Corrosion in Action" International Nickel films.

From Reservoir to the Pipeline, by Harry G. Byars of Atlantic Oil Co., Dallas, Texas.

Economics of Corrosion Control, by Victor Maxwell of Sun Oil Co., Beaumont, Texas.

Fundamental Approach to Corrosion Control Methods, by Otto Grosz of the California Co., New Orleans, La.

Corrosion Problems, Detection and Control Practices in Producing Operations, by Kelly H. Rench of Superior Oil Co., Lafayette, La.

Water Treatment: Water Flood, Disposal, Bacteria, Scale Corrosion Control, by Charlie Walker of Tretolite Co., St. Louis, Mo.

Thursday, June 8

Coatings for Offshore Structures, by Charles Fritz of Socony Paint Products Co., Houston, Texas.

Cathodic Protection of Offshore Structures, by J. L. Andrews National Electric Manufacturing Co., Houston, Texas.

Cathodic Protection of Well Casing,

Vessels, Pipelines and Plants, by W. H. Stewart of Sun Oil Co., Beaumont, Texas.

Internal Coatings, by Len Edgar of Tube-Kote Co., Houston, Texas.

Corrosion Inhibitors, Field Application, Evaluation and Laboratory Testing, by E. D. Junkin of Tidewater Oil Co., Houston, Texas.

Use of Coatings for Paraffin Control, by Luther Ellison of Sun Oil Co., Dallas.

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Teche Section scheduled a panel discussion on high pressure gas well treating techniques at its May 3 meeting.

Panel discussion on completion fluids was participated in by Kelly Roach of Superior Oil Company, R. S. Baker of Drilling Specialties Company and Parke Muir of Dow Chemical Company at the April 12 meeting.

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East Texas Section heard H. C. Noe, Jr., of Visco Products Company, Inc., speak on inhibitor squeezes at its April 25 meeting.

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Greater Baton Rouge Section scheduled a talk on stainless steel corrosion by R. J. Jurry of Union Steel Corporation for its May 21 meeting.

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Alamo Section heard Carl T. Stevens of Minneapolis-Honeywell Regulator Company speak on instrumentation and related problems of corrosion at the April 11 meeting.

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Tulsa Section at the April 24 meeting heard Charles M. Hudgins. Jr., of Continental Oil Company speak on corrosion problems in the use of dense salt solutions as packer fluids.

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West Kansas Section will meet September 7, October 5, November 2 and December 7.

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North Texas Section has appointed K. D. Wahlquist of Southern Union Gas Company, Dallas, Texas, interim chairman to serve out the term of J. R. McIntyre of Atlantic Refining Company, Dallas, Texas, who has resigned as section chairman.

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The 1961 South Central Region Conference and Exhibition will be held October 24-26 at the Shamrock-Hilton Hotel, Houston, Texas.

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DIV

Northeast Region

Gackenbach   E. G. Holmberg

Gackenbach Heads New York Conference Committees

General chairman for the 13th Annual Northeast Region Conference is Russell E. Gackenbach of American Cyanamid Company, New York, N. Y. Technical Program Chairman is Emil G. Holmberg of International Nickel Company, Inc., New York, N. Y.

Other conference chairmen are Publicity and Printing—Jack Lloyd of Subox, Inc., Hackensack, N. J., Local Arrangements—A. F. Minor of American Telephone and Telegraph Company, New York, N. Y., and A. L. Ayres of New Jersey Bell Telephone Company, Newark, N. J., Finance—Joseph I. Montel of Hammond-Montel, Inc., Elmhurst, N. Y., and Field Trips—Robert B. Wooster of Duriron Company, Inc., New York, N. Y.

The conference will be held October 30-November 2 at Hotel Statler, New York City.

●

Pittsburgh Section scheduled a tour of Duquesne Brewery at Pittsburgh on May 4. Brewery representatives spoke on corrosion problems in the brewing industry.

●

Lehigh Valley Section elected officers for 1961-62 on April 17 at Reading, Pa. New officers are Chairman Ray R. Graver of Electrochemical Engineering and Manufacturing Company, Emmaus, Pa., Vice Chairman Donald H. Gittelman of Glidden Company, Reading, Pa., and Secretary-Treasurer William H. Rutter of Electrochemical Engineering and Manufacturing Company, Emmaus, Pa.

●

Greater Boston Section elected new officers at its April 12 meeting. They are Chairman W. S. Sanders, Vice Chairman J. R. Sarnosky and Secretary-Treasurer J. D. Buckley. John A. Gregory, Jr., of Hall Laboratories spoke on corrosion in boilers and condensate liners at the meeting.

Canadian Region

Toronto Section heard L. Garner of Pangborn Corporation speak on surface preparation by blast cleaning at its April 12 meeting. Thirty members and six guests were present.

Skilled Tube-Kote inspectors approve coating quality for each length of pipe prior to shipment.

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Canada

Western Region

D. D. McGregor Named General Chairman For October 3-5 Western Region Meeting

Don D. McGregor of the U. S. Corps of Engineers, Portland, Ore., is general chairman for the 1961 Western Region Conference to be held October 3-5 at the Benson Hotel, Portland, Ore.

Vice chairman for the conference is Otto L. Hudrlik of Nalco Chemical Co., Portland. Secretary is Samuel F. Grubb of Portco Corporation, Portland.

Technical program chairman is John Van Bladeren of Northwest Natural Gas Co., Portland.

Chairmen of the eight technical symposia included in the technical program are as follows:

Corrosion Principles: Keene R. Shogren of Northwest Natural Gas Co., Portland.

Materials: Dean D. Burgan of Electric Steel Co., Portland.

Building and Mechanical Equipment: Tai Funatake of Bruce Morrison Consulting Engineers, Portland.

Fresh Water: Robert S. Baynham of Dearborn Chemical Co., Portland.

Marine: Jim Norton of J. F. Norton Consulting Engineers, Seattle, Wash.

Utilities: W. H. Messenger of Pacific Telephone—Northwest, Portland.

Pulp and Paper: B. L. Bergman of Northwest Natural Gas Co., Portland.

George Silkworth of El Paso Natural Gas Co., Salt Lake City, Utah, will be chairman of another symposia.

Other conference committee chairmen are William H. Kipp, Jr., of Waterworks Supplies Co., Portland, local arrangements; John C. Moeller of Lloyd Corp., Portland, registration; Joseph R. Smith of Northwest Natural Gas Co., Portland, publicity and printing; and Leonard B. Freese of U. S. Corps of Engineers, Portland.

•

Portland Section program for April 13 included a talk and slide show on protective coatings field tested under various environments. Carol E. Maxwell of Sherwin-Williams Company gave the presentation, attended by 42 members and guests.

•

Los Angeles Section officers for 1961 are Chairman Phillip H. Burch of Products Research Company, Burbank, Cal., Vice Chairman Thomas J. Degnan of Pacific Lighting Gas Supply Company, Los Angeles, Cal., and Secretary-Treasurer Robert F. Flammang of Magna Products, Inc., Santa Fe Springs, Cal.

On May 17, L. L. Whiteneck, former president of NACE, discussed method for evaluation of protective coatings.

•

San Francisco Bay Area Section heard a talk on submerged and underground cathodic protection by R. Kent Lundergan of Electro-Rust Proofing Company on April 11 at Berkeley, Cal.

Hudrlik   McGregor

Baynham   Bergman   Messenger   Norton
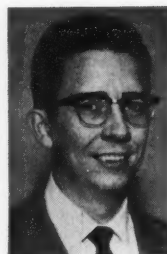
Burgan   Freese   Shogren   Silkworth

Funatake   Grubb   Smith   Van Bladeren

SECTION CALENDAR
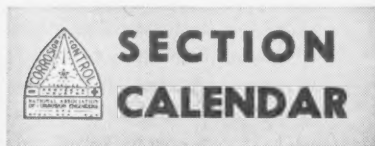
June
12   Central Oklahoma Section
13   Houston Section. Report on First International Congress on Metallic Corrosion held in London, by Norman Hackerman, University of Texas
15   Alamo Section
20   Chicago Section
26   New Orleans Section

July
5   Teche Section
18   Chicago Section
20   Alamo Section
31   New Orleans Section

Southeast Region

Seven Papers and Authors Given for Miami Conference

Seven papers have been scheduled for presentation at the 1961 Southeast Region Conference to be held in conjunction with the Florida General Conference Nov. 27-Dec. 1 at Key Biscayne Hotel, Miami, Fla.

Papers to be presented include the following: 37 Years of Cooperation—The Louisville Joint Electrolysis Committee by Stuart H. Gates, Soil Box Demonstration by M. C. Miller, Inorganic Pro-

Overseas Correspondents

Four reports on corrosion activities in Holland, Italy, India and Japan during 1960 are given below.

Holland

A symposium on Materials With Protective Coatings was held at Utrecht on May 13, 1960, by Bond voor Materialenkennis. Papers presented were Galvanic Coatings by P. Baeyens, Prosphating of Metal Articles by M. J. Reidt, Protection of Wood by Paint and Varnish by H. W. Talen and Protection of Iron by Paint by W. J. Nijveld. Papers presented by Talen and Nijveld were published in "Verfkroniek" 33 (1960), 356-359 and 349-355.

At Amsterdam on June 1-2, a symposium was held by Vereniging voor Oppervlaktetechnieken van Metalen. Metal surface finishing techniques were exhibited. Papers given included Possible Applications of Thermal Coatings by J. F. H. Eynsbergen, Possible Applications of Metal Spraying by W. Jansen and Possible Applications of Electroplating by P. Baeyens. These papers, excluding Baeyens', were published in "Galvanotechnik" 4 (1960), 56-57, 76-84 and 112-115.

During 1959 and 1960, Bond voor Materialenkennis held 10-week night courses on Corrosion and 12-week night courses on Practical Corrosion Problems in several cities.

Corrosion articles published in 1960 in Holland are listed below.

Investigations Into the Properties of a Number of Anti-Rust Coatings for Ship Bottoms by H. W. Talen, W. J. Pfeiffer and A. M. van Londen appeared in Publication 74 of the Metal Research Institute T.N.O. and Circular 94 of the Paint Research Institute T.N.O. (Reprinted from "Schip en Werf" 27 (1960), 271-285.)

Cathodic Protection Against Corrosion of Ship Bottoms—The Effect on Paint Systems by J. W. Boon appeared in Publication 75 of the Metal Research Institute T.N.O. (Reprinted from "Schip en Werf" 27 (1960), 304-312.)

Instruction Sheet on Metallic Corrosion Tests, instigated by the Netherlands Corrosion Center and carried out by the Corrosion Study Committee of Bond voor Materialenkennis, appeared in "Metalen" 15 (1960) 353-355 and "Polytechnisch Tijdschrift" 24 (1960), 1134a-1137a.

1960 Guide for Surface Treatment of Structural Steel, instigated by the Netherlands Corrosion Center and carried out by a task group in conjunction with Vereniging Metaalbeits (Metal Etching Association), appeared in "Metalen" 15 (1960), 390-393 and 407-409 and in "Schip en Werf" 27 (1960), 671-675.

Glass Wool as Filler in Wrapping of Steel Pipe (report of Corrosion Committee II) by J. F. Bogtstra appeared in "Het Gas" 80 (1960), 204-210.

All papers and publications are printed in Dutch.

W. J. Pfeiffer, Dutch Correspondent
Corrosion Institute T.N.O.
Afedling Corrosie
Postbus 52
Delft, Netherlands

Italy

In the Electrochemical Laboratory at the Politecnico di Milano, research on electrochemical behavior of metallic single crystals was extended to include copper and gold.

Overvoltages in exchanges of either electrode metal ions or hydrogen ions have been measured; several typical conditions have been characterized. Utilization of single crystals as electrodes of oriented surfaces appears very important because of the problem of the anisotropy of the kinetic electrochemical behavior; it is also the most natural way to control the electrode structure to attain definite and reproducible results in precision investigations.

Main results of this work have been published in "Rendiconti Istituto Lombardo Scienze e Lettere," "Rend. Accad. Naz. Lincei," and "Metallurgia Italiana." A comprehensive monograph will be published at the end of the present program.

The part of the work sponsored by Air Research Development Command, USAF, through European Bureau in Brussells by Contract AF 61(052)-144 is given in several technical notes and reports.

The book "Elementi di Teoria Della Corrosione a Umido Dei Materiali Metallici" by R. Piontelli has been published by Longanesi of Milan. Containing 452 pages, 43 figures and 11 tables, the book covers general definitions of corrosion terms and concepts (50 pages), thermodynamics and kinetics (230 pages), main factors involved in corrosion phenomena, etc.

In October at the University of Ferrara, a successful international meeting on corrosion inhibitors, organized by L. Cavallaro, was held. Proceedings of the symposium will be available shortly.

Systematic work on oxygen reduction processes and several other topics correlated with corrosion has been carried out by G. Bianchi and co-workers in the Chemistry Department of Milan University.

R. Piontelli, Italian Correspondent
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India

Scientists in India were quite active in the anti-corrosion field during 1960. The Electrochemistry Laboratory of the India Institute of Science at Bangalore and the Central Electrochemical Research Institute at Karaikudi continued to be the most active research centers. Corrosion was one of the major branches of electrochemistry covered by the Bulletin of the India Section of the Electrochemical Society. The India Section released the publication "Symposium on Electrodeposition and Metal Finishing" (188 pages, 1960) containing 36 papers on metal finishing and corrosion.

Two seminars in electrochemistry and

Wrong Holmberg Photo Published in May Issue

A photograph of E. G. Holmberg was printed on Page 62 of the May issue of CORROSION by mistake instead of a photograph of M. E. Holmberg, who has been nominated for election to the NACE Board of Directors as representative for active members.

M. E. Holmberg, an NACE member since 1945, is a metallurgical consultant of Houston, Texas, working on metallurgical and corrosion problems related to the oil and petroleum industries. He was associated with Phillips Petroleum Company for 15 years before opening his own consulting offices.

M. E. Holmberg

By coincidence, the photograph of E. G. Holmberg also appears in this issue—on Page 56. He is serving as technical program chairman for the Northeast Region Conference to be held October 30-November 2 in New York City. E. G. Holmberg is associated with International Nickel Co., Inc., New York, N. Y.

Complete File of 1950-60 Corrosion Issues Available

A complete file of back issues of CORROSION for the 11 years 1950-60 inclusive is available from F. C. Jelen, 1920 Glenwood Ave., Syracuse 4, N.Y. The years 1950-54 inclusive have had advertising pages removed while those for 1955-60 inclusive are complete with all pages.

Anyone interested in getting this file is invited to write to Mr. Jelen.

Southeast Region

tective Coatings by C. G. Munger, Stress Corrosion of Cast Aluminum Alloys by F. M. Reinhart, Stress Corrosion of Aluminum-Magnesium Alloys by Lee Craig, Armco 17-7 PH High Strength Stainless Steel by J. J. Halbig and Cathodic Protection of Bridge Strand in Sea Water by Jane H. Rigo.

NACE President E. C. Greco will give the opening address.

Birmingham Section on September 8 will be addressed by R. W. Ackermann, senior engineer, Central Area Office, of American Telephone & Telegraph Company, Cincinnati, Ohio. Mr. Ackermann's present assignment is handling corrosion, lightning and electrical coordination matters.

Title of his address will be Utilization of Schematic Circuits and Field Experiments for Interpreting the Significance and Reliability of Electrical Tests Results in Determining Corrosion Susceptibility of Buried Metallic Structures.

For the past several years Mr. Ackermann, a NACE member, has been a speaker at the Annual Appalachian Underground Corrosion Short Course.

Overseas Correspondents—

a corrosion refresher course were arranged at the CECRI, Karaikudi. The National Metallurgical Laboratory at Jamshedpur held a symposium on Light Metal Industry in India, which included a section on corrosion resistance properties. The Indian Standards Institution at New Delhi has set up a panel for corrosion research of light-guage steel structures.

Technical papers relating to corrosion and allied topics were presented at meetings and conferences held in India and abroad. The following papers were presented abroad: (a) At the Symposium on Inhibitors, 16th Annual Conference of the National Association of Corrosion Engineers held at Dallas, Texas, USA—Inhibition of the Corrosion of Commercial Aluminum in Alkaline Solutions by J. Sundararajan and T. L. Rama Char, Bangalore, (b) At the European Symposium on Corrosion Inhibitors held at Ferrara, Italy—Inhibition of the Corrosion of Pure Aluminum in Sodium Hydroxide Solutions by J. Sundararajan and T. L. Rama Char, and Studies on Mechanism of Corrosion Inhibition at the Central Electrochemical Research Institute, Karaikudi, by K. S. Rajagopalan, Karaikudi and (c) At the Symposium on Corrosion, 118th meeting of the Electrochemical Society, Houston, Texas, USA—Inbibition of Corrosion of Pure Aluminum in Hydrochloric Acid Solutions by J. Sundararajan and T. L. Rama Char, Bangalore.

The activities in 1960 were centered on fundamental studies, corrosion inhibition—immersed conditions and vapor phase, anodic corrosion and passivity, cathodic protection and protective coatings. Twenty-eight papers on corrosion and allied fields were published in Indian and foreign journals.

T. L. Rama Char
Indian Correspondent
Electrochemistry Laboratory
Indian Institute of Science
Bangalore 12, India

Japan

Corrosion activities in Japan during 1960 included the following:

Corrosion Committee of the Japan Society for Promotion of Science (K. Ishimura, Chairman)

Committee members, supporting members and associate members number 50, 65 and 590 respectively. Eleven meetings were held during 1960, at which 35 reports on corrosion were presented. This group Publishes "Corrosion Engineering" (12 issues a year).

A two-day corrosion symposium was held in November, at which the following papers were presented:

1. Study of Lead Alloy Anodes for Cathodic Protection (on anodic corrosion of lead and lead alloys in sulphuric acid solution).

2. Polarization Potential of Metal and Faraday Impedance (Part 2) (Interfacial Impedance Characteristics of Various Metals).

3. Effects of Temperature and Agitation on Protective Potential of Steels.

4. Cathodic Protection of Pipe-Type Cable.

5. Simple Calculation Method for Cathodic Protection of Inside of Steel Pipes

6. Peculiarity of Cathodically Protected Construction of Buried Pipe Lines in Japan.

7. Usefulness of Zinc Anode.

8. Corrosion of Tanks of Tankers and Its Countermeasure (Part 1).

9. Some Considerations on Cathodic Protection of Ballast Tanks of Tankers

10. Cathodic Protection by zinc at Peak Tanks and Double Bottoms of Cargo Boats.

---

11. Protection of Cavitation-Erosion of Copper Alloys in Sea Water.

12. Optimum Protective Potential of Copper Alloys to Cavitation in Sea Water.

13. Usefulness of Rust Preventive Paints for Steel Products.

14. Corrosion Resisting Property of Aluminized Steels in Various Aqueous Solutions.

Subjects of discussion were Protective Paintings for Iron Structures Exposed to the Atmosphere, and Cavitation-Erosion and Erosion-Corrosion.

Electric Corrosion Control Committee (Y. Takamura, Chairman. Eighty committee members)

The following subjects were taken up by the subcommittees for extensive study: Corrosion of Electric Railways, Stray Current Corrosion, Corrosion of Lead Cable Sheaths, Underground Corrosion of Buried Pipes, and Protection of Buried Iron and Steel Pipes by Means of Paint Sheating.

Japan Corrosion Engineer's Association (S. Inouye, Chairman. H. Sugano, Acting Chairman)

The committee and a few subcommittees held meetings for making drafts for the standard of measurement of corrosion of metals, qualities of corrosion preventive oils, vaporizable inhibitors and anti-corrosion packings. Meetings for lecture and short course were held in order to popularize the knowledge on corrosion of metals. This group publishes "Corrosion Control" (12 issues a year).

Electrochemical Corrosion Prevention Committee (G. Okamoto, Chairman)

The committee meetings were held three

times during 1960 to discuss theoretical aspects of electrochemical corrosion.

Association of Surface Treatment of Metals (V. Hashimoto, Chairman)

To commemorate the 10th anniversary of the association, several meetings for lecture and short course were held to promote practical knowledge on plating, metallicon and other surface treatments.

Light Alloy Association

Committee meetings were held to discuss various subjects on surface treatment and application of magnesium anode.

Shipbuilding Research Association on Corrosion

Committee meetings were held to discuss protection of ship body and problems on corrosion by fuel oils.

Corrosion Committee of Petroleum Society

The committee undertook to investigate corrosion in oil refineries.

Corrosion Symposium Between Technical Societies

The Electrochemical Society and the Japan Institute for Metals held a joint corrosion symposium in October at which 27 papers on corrosion and the prevention thereof were presented.

The Japan Institute for Metals held two lecture meetings during the spring and fall of 1960 to discuss various corrosion problems.

<div align="right">

T. Fujiwara
Japanese Correspondent
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Central Building
2-1 Chome Kyobashi
Chuo-Ku, Tokyo, Japan

</div>

Technical Articles Scheduled for Publication

Method for Prevention of Hydrogen Embrittlement of Tantalum in Aqueous Media, by Claude R. Bishop and Milton Stern

Corrosion of Lead Cable Sheath, by K. G. Compton

Use of Pipe-to-Soil Potential in Analyzing Underground Corrosion Problems, by B. Husock

A New Coatings Material for Corrosion Control, by B. H. Mahlman and E. J. Kaatz

Use of Differential Thermal Analysis in Exploring Minimum Temperature Limits of Oil-Ash Corrosion, by Norman D. Phillips and Charles L. Wagoner

Microbiological Corrosion in Waterfloods, by J. M. Sharpley

Corrosion Control Methods in Desert-Like Areas, by W. C. R. Whalley

Problems Encountered in an Ammonia Absorption System, by R. B. McIntosh

$10,000. in Awards for Hot Dip Galvanizing Ideas

Ten awards offered by American Hot Dip Galvanizers Association in cooperation with American Zinc Institute

Galvanizers International Award

THINK! Think about new uses for Hot Dip Galvanizing! Or, improvements in present uses! Or, new methods of after treatment! If your idea is accepted, you will receive one of ten awards of $1000 in cash, plus a handsome medal, plus an engrossed Certificate of Achievement.

Not a contest but a search for new ideas

This is not a contest—it is a search for new ideas. Your entry will not be judged against others, but solely on its merit and value in developing new applications and markets for Hot Dip Galvanizing. If your idea, in the opinion of the judges, is of practical value to the industry, you will be cited for an award—promptly.

The Hot Dip Galvanizing Industry is anxious to receive ideas of this type; therefore, the judges reserve the right to present *more than 10 awards*, if the entries warrant.

These well-known men will act as judges

Dr. Clarence H. Lorig, Technical Director, Battelle Memorial Institute and Past President American Society for Metals. Mr. John R. Daesen, Technical Director, American Hot Dip Galvanizers Association. Mr.

John L. Kimberley, Executive Vice President, American Zinc Institute.

Anyone is eligible to enter

Anyone in the world (except members of the American Hot Dip Galvanizers Association and the American Zinc Institute, and their employees and advertising agencies) may submit one or more entries.

Business firms or corporations may submit entries under their business name, instead of as individuals, if they choose.

Entries will be considered by the judges promptly upon their receipt. No entry received after April 30, 1962 will be considered.

These are the kind of ideas we're looking for:

The Awards will be made for ideas pertaining to: (a) Applications of Hot Dip Galvanizing to a new or unusual field, or; (b) An improvement in application in fields where Hot Dip Galvanizing is now being used, or; (c) New methods of aftertreatment of Hot Dip Galvanized products.

Each entry must contain:

(a) Description and documentation of application.

(b) Case history of the applica-

tion or process accompanied by photo, drawings, formulae, etc.

(c) All technical data needed for the utilization of the idea submitted.

(d) Release of the application or idea for general use without payment or royalty other than the $1000 award.

Other conditions:

The decision of the judges will be final.

Award-winning ideas will be retained by the American Hot Dip Galvanizers Association for dissemination throughout industry. Other entries will be returned.

No formal entry blank is required. The entry should be accompanied by your name, address and business connection.

Entries should be sent to:

AMERICAN HOT DIP
GALVANIZERS
ASSOCIATION, INC.
5225 Manning Place, N. W.,
Washington 16, D. C.

Note: For information on galvanizing, write to the above address for name and location of the American Hot Dip Galvanizers Association member nearest you.

INDEX TO CORROSION ABSTRACTS

Vol. 17   June, 1961   No. 6

4. CORROSIVE ENVIRONMENTS

4.2 Atmospheric

4.2.3, 6.3.10
Studies in the Chemistry of the Operation of Solid-Fuel-Fired Gas-Turbines. Pt. V. Dry-Corrosion Aspects of Peat-Ash Deposition. J. A. Waddams, J. C. Wright and P. S. Gray. J. Inst. Fuel, 32, No. 220, 246-249 (1959).

The dry corrosion of Nimonic 80A turbine blades by components of peat ash is described. The most corrosive substances present are Na_2SO_4, K_2SO_4, and NaCl. Addition of NaCl to the sulfates gives a marked increase in the rate of corrosion. $Ca_3(PO)_4$, $CaSO_4$, Na_2HPO_4, and Na_2SiO_3 are only moderately corrosive, although molten Na_2SiO_3 fluxes the protective Cr_2O_3 film, allowing further oxidation to occur. The protective Cr_2O_3 film is disrupted in the presence of NaCl leaving the underlying metal vulnerable to attack. The alkali sulfates are reduced to sulfides at the interface between the Ni-Cr solid solution and the sulfates, and the sulfur ions diffuse into the matrix at $\sim$ 800 C leading to catastropic corrosion.—MA.   20150

4.2.1, 2.2.2, 6.2.3, 3.5.9
Atmospheric Factors Affecting the Corrosion of Steel. P. J. Sereda. Ind. & Eng. Chem., 52, No. 2, 157-160 (1960) Feb.

Recent development of a method of detecting moisture on exposed steel samples has made it possible to determine readily the time during which such samples are wet. When this measurement is used as time base for calculating corrosion rate, influence of other two major factors, SO_2 and temperature, can be more clearly established. Correlation obtained on this basis for outdoor exposure of low-carbon plain steel at two sites at Ottawa, Canada, shows a well-defined increase in corrosion rate with increase in temperature and in SO_2

pollution rate. This approach shows promise as a method of rating corrosivity of any inland exposure site. Composition of steel samples exposed is tabulated and include 0.048 nickel. Graphs, tables, 15 references.—INCO.   19980

4.2.3, 7.1
Industry's Battle with Fuel Ash. R. C. Bellas. Power, 104, No. 4, 83-88 (1960) April.

Describes how slag deposits and corrosion attack in high-temperature zones of combustion equipment (alkali sulfates and vanadium) and corrosion by residual-oil ash in low-temperature areas (formation of H_2SO_3 and H_2SO_4 due to combustion products SO_2 and SO_3); and reviews measures taken by industry to prevent these problems. In addition to oil-fired units, reference is made to coal-fired boilers, gas turbines, and diesel engines.—INCO.   20146

4.4 Chemicals, Organic

4.4.7, 6.3.6, 5.5.1, 6.3.8
Studies of the Corrosion Behavior of Non-Drying Oils and Greases, with Special Consideration of Modern Lubricants and Metal Preservatives. Pts. I, II, III. (In German.) A Bukowiecki. Schweiz. Arch. angew. Wiss. Techn., 25, Nos. 1, 2, 3; 23-34, 62-74, 96-101 (1959).

I. The attack of sulfur-bearing oils on copper alloys was studied; many alloys, including 60:40 brass, are less readily attacked than pure copper, tin bronze or silver. The attack of heavy-duty and engine oils on lead-bronze bearings was studied by weight-loss determination on lead and copper plates immersed in oils at 140 C together with iron plates; in a covered vessel the retention of volatile acids greatly intensifies attack on lead. Similar tests were carried out on pieces from lead-bronze bearings protected by thin layers of nickel, lead-tin alloy, tin, indium, lead-indium alloy, and with linings of lead-indium alloy and white metal. The weight-losses in various oils were very low compared with those of lead plates, but bronzes with $\sim$ 50% lead suffered appreciable attack in spite of tin or indium coatings.
II. Metal discs were immersed in oil containing 5% water at room temperature for 3 and 24 months; the effect of 0.1% acetic and stearic acid in the oil was also tested. The former accentuates corrosion of iron, copper, lead and zinc, the latter inhibits it. Similar tests on the same metals as well as cadmium- and tin-plated steel were carried out with water-containing Diesel fuels; lead and zinc were more heavily attacked than iron, but copper also suffered detectable weight-losses.
III. The factors determining corrosion and protection by oils and greases are considered and the literature is reviewed. Experimental work on grease films and the effect of inhibitors is reviewed.—MA.   20124

4.4.7, 4.4.2, 6.3.6, 4.4.9, 5.8.4
Studies of the Corrosion Behavior of Non-Drying Oils and Greases, with Special Reference to Modern Lubricants and Inhibitors. A. Bukowiecki. Schweiz. Arch. angew. Wiss. Techn., 24, Nos. 7,

8, 9; 201-217, 263-270, 295-303 (1958) July, Aug., Sept.

Decomposition and oxidation of some oils and greases produce organic acids which may have corrosive, or sometimes inhibiting, effects. Bearing shells in internal-combusion engines of lead bronzes and some cadmium alloys are particularly susceptible to attack by such products. Some lubricants contain sulfur compounds which may attack copper and its alloys at elevated temperatures. Short-time tests on copper strip can be misleading. Organic chlorine compounds and water dispersions also have corrosive effects. Strips of various metals and alloys were bent to present a raised surface, and the effect of placing a spot of oil or grease in an indentation on this surface was assessed. The response of copper, lead, zinc and aluminum to four oils, and of copper to several greases, is tabulated. Two pastes with MoS_2 addition were highly corrosive owing to the presence of sulfuric acid.—MA.
19978

4.4.7, 5.8.1, 5.5.3
In Situ Conversion of Operating Hydraulic Oils to Preservative Oils. R. L. LeMar. Rock Island Arsenal Lab., Rept. No. 59-2773, October 26, 1959, 19 pp. Order PB 145114 from Library of Congress, Photoduplication Service, Publications Board Project, Washington 25, D. C.

Fourteen commercial, inhibitor, additive concentrates were evaluated in four

samples of used, operating hydraulic oil. A number of these concentrates were found to convert such an oil to an inhibited oil with preservative properties comparable to MIL-L-21260 oil. These additive concentrates were also miscible with the oil at room temperature and so could be added directly to the oil in the machine tool hydraulic system and mixed therein, by exercising the machine tool. Viscosity and flash point effects of the additive concentrates were also considered. A list of quality control tests for future selection of concentrates is included. (auth.)—GRR. 19887

4.7 Molten Metals and Fused Compounds

4.7, 8.4.5
Molten Salts in Nuclear Reactors. (Bibliography.) (In French.) J. Dirian and R. Saint-James. Commissariat à L'Énergie Atomique, Paris, France. Rept. CEA-1194, 1959, 33 pp. On Deposit in the Depository Libraries.

References relating to the corrosion of materials by these salts are included and the treatment of the salts with a view to recovery after irradiation in a nuclear reactor is discussed. (auth.)—NSA. 20202

4.7, 8.9.1, 3.7.2
Further Investigation of the Effects of Molten Boron Oxide on High Temperature Materials. Joseph W. Rosenbery. U. S. Wright Air Development

Center, Technical Rept. 59-205, May 1, 1959, 101 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

Corrosion resistance of a group of high-temperature materials, typical of those available for use in aircraft power plants, was evaluated in a boron oxide environment. Exposure consisted of cyclic immersion in B_2O_3 at 1750 to 2200 F for periods up to 145 hours in an air atmosphere. The results indicate aluminum, manganese, and carbon as alloy constituents are detrimental to corrosion resistance, while silicon appears to produce beneficial effects. Several possible mechanisms of attack by molten boron oxide are postulated to expain the data. (auth.)—NSA. 19929

4.7, 2.1.1, 3.8.4
Some Calculations of Diffusion Controlled Thermal Gradient Mass Transfer. J. J. Keyes, Jr. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-57-7-115, July 22, 1957 (Declassified October 9, 1959), 43 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

Calculations are presented of the amount of mass transfer to be expected in liquid alkali metal-Ni alloy systems for two assumed diffusion mechanisms. In one, the boundary layer is assumed saturated and the transfer rate is limited by the rate of diffusion of solute into the liquid. In the other, the mass transfer rate is assumed to be limited by the

diffusion rate of a component of the solid alloy to the solid surface. It is concluded that a more general hypothesis is needed.—NSA. 19936

4.7, 6.2.2
Attack of Molten Zinc on Iron—A Summary. (In German, English translation available.) K. Ruttewit. Metall **13**, No. 8, 735-738 (1959) Aug.

As well as summarizing previous research by Horstmann, Bablik and other workers on the attack of molten zinc on iron, the author describes experimental work carried out by himself and his colleagues. One of their results differs from Horstmann's findings in that 3 crystals occurred above 495 C. The attack on iron of molten zinc with deliberate additions is to be examined in a further article. 3 figures, 4 illustrations.—ZDA. 19901

4.7, 6.3.9, 6.3.16
Effect of Nitrato-Nitrite Molten Mixture and Its Compounds on Molybdenum, Tungsten, Zirconium, Tantalum and Columbium. (In Russian.) E. I. Gurovich and G. P. Shtokman. J. Applied Chem. (Zhur. Prikladnoi Khim.), **32**, 2673-2677 (1959) Dec.

High-purity molybdenum, tungsten, zirconium, tantalum and niobium are corrosion tested in melt of nitrato-nitrite mixture at 100-600 C. Molybdenum and tungsten are observed to be the least corrosion resistant and it is recommended that these metals not be used as alloying elements in steels which come into contact with nitrates, nitrites or their mixtures. 4 references. —RML. 20076

5. PREVENTIVE MEASURES

5.3 Metallic Coatings

5.3.4
Progress Towards the Development of a Non-Embrittling Cadmium Electroplating Process. Pt. II. Use of Aliphatic Amino Acids as Complexing Agents in Aqueous Baths. P. N. Vlannes and S. W. Strauss. Plating, **46**, No. 9, 1046-1051 (1959).

Vlannes and Strauss discuss plating baths containing six aliphatic mono-amino acids over the range pH 7-10. Delayed-fracture tests indicate that these baths are less embrittling than the cyanide bath, optimum results being obtained with glycine and α-amino-n-butyrate. Throwing-power measurements were inconclusive since results depended on the method used, but throwing power was invariably superior during barrel plating.—MA. 19957

5.3.4
Progress Toward the Development of a Non-Embrittling Cadmium Electroplating Process. Pt. III. The Use of Triethanolamine in Cadmium Plating Solutions. P. N. Vlannes, S. W. Strauss and B. F. Brown. Plating, **46**, No. 10, 1153-1157 (1959).

Non-cyanide aqueous baths containing triethanolamine with and without glycine, were investigated over a wide range of pH and composition. Current density characteristics were obtained in the Hull cell, and barrel-plating tests showed that continuous plating for 30 days was possible without replenishment of the electrolyte. The triethanolamine bath is non-embrittling, under conditions of controlled current density, as judged by the delayed fracture test.—MA. 19958

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5.3.4

Plating with Duplex Chromium. Edgar J. Seyb, Jr. Precision Metal Molding, **17**, No. 9, 71-73 (1959).

Corrosion is greatly reduced by depositing a finely cracked chromium layer on top of crack-free chromium. The many cracks disperse the cell action over a large area, hence current density is below the critical potential for anodic performance of the underlying metals. The method of application is given.—MA. 19960

5.5.3, 2.3.2

Development of an Internal Preservative Oil for Machine Tools. R. LeMar. Rock Island Arsenal Lab. Rept. No. 59-3003, November 24, 1959, 32 pp. Order PB 145115 from Library of Congress, Photoduplication Service, Publications Board Project, Washington 25, D. C.

Experimental work was carried out to develop oil formulations whose corrosion preventive properties approached those of Military Specification MIL-C-14201A, Grade 1, "Corrosion Preventive, Soft-Film, Cold Application," and would be suitable as an internal preservative for machine tools. A number of accelerated corrosion tests were evaluated to find methods suitable for the reasonably rapid testing of highly inhibited, heavy, long-term preservative oils. In the course of these tests it was shown that cyclic accelerated corrosion tests can show very poor performance characteristics for oils that perform well in constant temperature and constant humidity tests. These test results on the RIA blends provided a basis for the preparation of a list of test methods and requirements to define the proposed long-term internal preservative oil for machine tools. 5 references.—GRR. 19943

5.3.4

Influence of Urea on the Electrolytic Deposition of Nickel. (In German.) W. Machu and M. F. M. El-Ghandour. National Research Center, Cairo-Dokki, Egypt, UAR. Werkstoffe u. Korrosion, **11**, No. 5, 283-286 (1960) May.

Urea has a highly detrimental effect on the current yield of a nickel bath as the yield is reduced to less than 50%. The presence of urea gives rise to higher polarizations which can be only partially reduced by increasing the temperature and current density. With a urea addition, however, it is possible, at low pH values of the bath, to obtain good nickel deposits even with comparatively low nickel salt concentrations and even with high current densities of 20 amps/dm^2. The brightness of the nickel coating is considerably improved by urea. 19840

5.3.2

Effect of Protective Coatings on the Properties of Ferritic Steel at 650°C. K. W. Mitchell, H. King and E. A. Brandes. Metallurgia, **61**, No. 363, 15-23 (1960) Jan.

Prevention of oxidation and scaling of steel by deposition of a protective coating of Al or Cr results in extended life under creep or fatigue stresses, providing that any softening of steel produced by coating process is more than compensated for by improved oxidation resistance. Results are presented of tests on 12 s. w. g. sheet in mild steel (En. 2A) and Mo-B, Mo-V, and Cr-Mo-V-W (0.70 Ni) low alloy ferritic steels. Al coatings were applied by hot-dipping and by metal spraying followed by a

diffusion treatment (aluminizing), and Cr coatings by deposition from Cr chloride vapor with simultaneous diffusion. Chromizing had an adverse effect on core strength—of decreasing importance with increase in thickness of core material—and suggestions are made for minimizing this effect by modification of process. Diagrams, graphs, numerous tables (particularly of tensile and creep properties) and photomicrographs.—INCO.   19823

5.3.4

Preparation and Properties of Iron-Nickel Films. I. Tsu. Plating, **47**, No. 6, 632-633 (1960) June.

Describes chloride plating bath from which iron-rich iron-nickel films having low coercive forces can be deposited. These iron-rich films become more anisotropic as nickel content increases. Nickel contents of films plated from given chloride bath can range from few percent to 95% due to addition of trace (0.2 g/l) of thiourea. Magnetic properties of nickel-rich films (95%) from chloride bath differ from those plated from Wolf's bath. Former films showed high degree of anisotropy and low H_c as compared to high H_c and negligible anisotropy observed in 95 Ni films from Wolf's bath. These studies demonstrate that anisotropy of iron-nickel films does not depend entirely on alloy composition of films. Graphs show influence of film composition on wall motion coercive force; and anisotropy imposed by applying magnetic field $>$ H_c in any direction. Table.—INCO.   19965

5.3.4, 2.2.5, 2.3.2, 8.8.5

Data on the Corrosion Resistance of Electroplated Zinz Die Castings. W. H. Safranek, H. R. Miller, R. W. Hardy and C. L. Faust. Battelle Memorial Inst. Paper before Am. Zinc Inst. Symposium, Detroit, Nov. 11-12, 1959. Plating, **47**, No. 4, 405-411 (1960) April.

Summarizes 3 programs on search for practical methods of improving corrosion resistance of electrodeposited zinc die castings. Program I investigated effect of increase in thickness of copper and nickel plate, and included study of crack free chromium and evaluation of cobalt and cobalt-nickel electroplates. Effect on corrosion of substituting electropolishing and leveling zinc plating for mechanical buffing was appraised. Program II continued study of crack-free chromium and included investigation of performance of duplex nickel coatings, and additional studies on effect changing thickness of copper and nickel plates. Stainless steel and anodized aluminum were included for comparison. Program III covered effects of different thickness of duplex nickel and crackfree chromium, and evaluated composites consisting of chromium-nickel-chromium, bright nickel-duplex chromium, and duplex nickel-duplex chromium. Accelerated tests used were Corrodkote, acetic acid salt spray, and CASS tests. Outdoor exposure sites were at Kure Beach,

Detroit and Columbus. Data show that duplex nickel coatings are efficacious, but perform effectively only when they are plated with 0.02 mil, or more, of chromium. Composite of bright nickel and 0.055 mil chromium was effective also in preventing corrosion during accelerated tests and outdoor exposure. Tables and graphs summarize ratings.—INCO.   19972

5.3.4, 6.3.9, 3.5.9

Adhesion of Electrodeposited Nickel to Chromium at Elevated Temperatures. Walter E. Reid, Jr. and Felding Ogburn. J. Electrochem. Soc., **107**, 91-93 (1960) Feb.

Use of a composite coating of electrodeposited nickel and chromium to protect molybdenum from oxidation at 800 to 1200 C exhibited certain practical limitations. Examination of the composite coating showed that the problems of blister formation, weakening of the bond between nickel and chromium, and edge separation were interrelated. Blister formation was eliminated and edge separation reduced slightly by an improved treatment of the chromium surface prior to nickel plating. The weakening of the bond between nickel and chromium appears to be inherent in the coating system. (auth)—NSA.   19998

5.3.4

Introduce Roller Burnishing Before Chromium Plating of Highly-Stressed Steel. (In Russian.) G. P. Kotlyarevsky, Metalloved i Obrabotka Metallov, No. 7, 52-53 (1958).

Endurance limits (10^7 cycles) of 9.48-mm.-dia. specimens of 08, 45, and 40KhN steels were 23, 24, and 35 kg./mm.^{2}, resp.; those of Cr-plated specimens (9.28 mm. core dia., Cr deposit 0.1 mm.), 12, 12, 21 kg./mm.^{2}, resp.; and those of similar Cr-plated specimens previously work-hardened by rolling of the surface were 26, 24, 28 kg./mm.^{2}, resp. A series of service tests on pump rods showed that those plated with 0.076-0.095 mm. Cr after surface rolling had the best wear-resistance and corrosion-fatigue behaviour.—MA.   19797

5.4 Non-Metallic Coatings and Paints

5.4.2, 5.4.8

Corrosion Resistance of Vitreous Enamel. N. S. C Millar. Bull. Institute of Vitreous Enamellers., **10**, 345-350 (1960) April.

Effect of mill additions, silica and titania content and aging on acid and weather resistance. Alkali resistance can be improved by adding alumina or zircon. Detergent concentration, temperature, fineness of grinding of the enamel slurry and under and overfiring affect detergent resistance. —RML.   20066

5.4.5, 5.3.4

Anti-Corrosive Water-Emulsion Paint for Metal Surfaces, Especially New Galvanized Steel. D. Frank. J. Oil & Colour Chemists' Assoc., **43**, 140-148 (1960) Feb.

Well-known difficulties encountered in the preparation and decoration of new galvanized steel surfaces may be overcome by the use of a special oil-free polyacrylic dispersion paint formulated with a correct pigment-binder ratio to assure durability and containing zinc chromate to inhibit corrosion. The paint exhibits remarkable durability, versatility, cheapness, and ease of application.—BTR.   20156

5.4.5, 6.2.1

Pigments for Protective Paints. (In German.) K. A. Oeferen. Metalloberfläche, **14**, 18-20 (1960).

Corrosion protection of steel and iron by minium, cyanide of lead, white lead, zinc white, zinc oxide, iron mica, Tidioxide, Al and Si carbide. 3 references. —RML.   19860

5.4.8

Anticorrosive and Marine Paints. J. C. Kingcome. Paint Mfg., **30**, 59-62 (1960) Feb.

A brief review of recent literature on anti-corrosive and marine paints covers urethane coatings, hot and cold bitumen coatings, primers, paints for aluminum, marine anticorrosive paints, and antifouling paints. 24 references.   19802

5.4.5

Protection of Steel Forms Against Corrosion. I. I. Kiselev and I. M. Zheleznyak. Beton i Zhelezobeton (USSR), No. 10, 389 (1958). Translation No. 4448 by M. Slade, 4 pp., 1960, Available from Library of Congress, or Special Libraries Association.

Use of a plastic coating for protection of the surface of the metal moulds is recommended. Sheets of vinyl foil glued to the inner surface of the moulds eliminate all corrosion of the metal forms for up to two years, and even longer; make lubricating unnecessary since concrete never adheres to the vinyl foil; and yield a smooth, uniform, and clean surface of the reinforced-concrete products so that these can be used without any additional external or internal facing.—TT.   19940

5.4.5

Preparation of Steel Surfaces for Repainting. J. Hurst. Corrosion Technology, **5**, No. 10, 313-315, 342 (1958) Oct.; Also in Building Topics, **9**, No. 3, 5-10 (1958).

Ideal at which to aim is gradual buildup of paint thickness, achieved only by repainting at fairly regular intervals, while original paintwork is still in good condition. Removal of millscale, cleaning of rusted surfaces, removal of contaminants (soot, grease, oil, chemicals and sea salt), and use of paint removers, are topics considered.—INCO.   19856

5.4.8, 3.3.4

Surface Coating Vehicles with Built-In Fungistats. L. A. Goldblatt, L. L. Hopper and R. Y. Mayne. Paint, Varnish, Prod., **49**, No. 8, 44-46, 85 (1959).

Vehicles based on epoxy esters of tung oil fatty acids and potentially fungistatic acids (propionic, sorbic and undecylenic) and on tung oil/tripropionin were tested for resistance to mould growth by the filter paper test. Some of those containing propionic and sorbic acids were promising. The tung oil/tripropionin vehicle showed outstanding exterior durability.—RPI.   20190

5.4.2

Lubricating Properties of Lead-Monoxide-Base Coatings of Various Compositions at Temperatures to 1250 F. Harold E. Sliney. National Aeronautics and Space Administration, Memo 3-2-59E, Feb. 1959, 22 pp.

Lead monoxide was the component primarily responsible for the lubricating properties of various ceramic coatings studied. Other oxides in the formulations influenced such properties as softening points, adherence to metals, hardness, vitrifying tendencies, or chemical stability. Oxidation of the base metal during coating and elevated temperatures had important and often beneficial effects. Several of the coatings protected metals against adhesive wear at test temperatures at 75 to 1250 F. Friction coefficients ranged from 0.20 to 0.37 at 75 F and from 0.08 to 0.20 at 1250 F. The sliding velocity in all experiments was 430 ft/min. (auth)—NSA.   20181

5.4.5, 5.3.2, 6.2.3

No Maintenance in Four Years with Zinc-Vinyl Coating System. G. Weyermuller. Chem. Processing, **22**, No. 10, 101, 108 (1959) Oct.

Combination of inorganic zinc silicate coating (known as Dimetcote) as base, followed by a vinyl primer (Amercoat No. 86) and then two vinyl topcoats in color (Amercoat No. 33), was found outstanding for protecting structural steel in chemical plants subjected to severe atmospheric conditions. Success of coating system at Torrance, Calif, plant of Union Carbide Chemicals Co, where polyethylene and ethylene oxide are manufactured has prompted its extensive use at other Carbide plants, such as Sea Drift and Texas City, Tex. and South Charleston, West Virginia. Part of steel used at Torrance plant was coated with Zn coating at steel supplier's plant and part at job site. Although some sub-assemblies were riveted or welded, most of steel was erected and fastened with high-strength bolts. Although specifications for this type of construction usually require that bearing surface not be painted (to maintain proper frictional contact), zinc coating in this case actually increases coefficient of friction and, in addition, prevents corrosion on bearing surfaces. Photos.—INCO.   20221

5.4.5, 3.4.9

Blistering. H. Nienhaus. Ind. Lack. Betrieb, **27**, No. 9, 281-285 (1959).

Causes of paint film blistering in moist atmospheres are discussed. Blisters in general are of less than 3 mm diameter, contain a solution of pH about 4 and occur between undercoat and finishing coat, particularly on retouched surfaces: they are not often seen on car bonnets. There appears to be a simple connection between rise in atmospheric humidity and incidence of blistering, but, contrary to a belief which has been gaining currency, there is no connection between H bomb tests and blistering. The principal cause lies in contamination of the original metal surface and of subsequent lacquer coats with water-soluble deposits, from, e.g., poor pretreatment techniques, washing with hard water, etc., which give rise to an under-film pressure, due to osmosis, in moist atmospheres.—RPI.   19869

5.4.5

Strippable Coatings Keep Products Bright, Clean, Safe. R. J. Fabian. Materials in Design Eng., **49**, No. 5, 110-115 (1959).

Use of various types of cellulosic and vinyl resin strip coatings for protecting metal articles during storage and fabrication is considered. Methods are given for applying these coatings, including web-based vinyl resin coatings, and illustrations show the ease of application and removal.—RPI.   20250

5.4.5

Wash Primers. Z. Jedliński and J. Nowak. Przem. Chem., **38**, No. 3, 176-180 (1959).

A study of the influence of pigment grade and of the H_3PO_4 content upon the anticorrosive properties of wash primers based on polyvinyl butyral resins and zinc and lead chromes. The importance of the relationship between the pH of the wash primers and its anticorrosive characteristics has been determined. The change in pH value depends considerably on the grade of pigment used and on the amounts of H_3PO_4 and water added. The best pigments appear to be basic zinc chromates, especially $ZnCrO_4, Zn(OH)_2$. Measurement of the redox potential, following the mixing of wash primer components, permits the determination of the period in which the paint shows increased passivating properties. The optimum content of H_3PO_4 in wash primers was found to be 3-4%. In painting with anti-corrosive paints, the application of reactive primers considerably extends the protection period for painted objects. Wash primers protect steel products, stored in the open air, for several weeks.—RPI.   19935

5.4.8, 3.3.4

Fungicides in Surface Coatings. (In German.) H. Hirschfeld. Fette, Seifen, Anstrich., **61**, No. 12, 1233-1239 (1959).

Discusses the problem of finding effective measures to inhibit the attack of moulds on surface coatings. After a comparative discussion of various anti-fungus agents, the organic compounds of mercury, tin and copper are dealt with in detail. Their preparation methods, as well as their chemical and toxicological properties, are treated briefly. Their application and methods of incorporating them in various coating agents are explained fully.—RPI.   19930

5.4.5, 5.3.4

Coping with Peeling Paint on Galvanized Parts. J. A. Ahlers. Workbench Magazine, **1959**, 46-47, July/August.

Deals with the chief causes for paint failure of exposed galvanized parts and suggests the necessary remedial action. Failures are chiefly due to painting in cold weather, wrong cleaning of the galvanized parts or the use of unsuitable paints. The author discusses the use of a metallic zinc paint, M.Z.P., and claims that it gives the best protection to galvanized parts. The paint is pigmented with 80% zinc dust and 20% zinc oxide. Advice is given on the renovation of galvanized parts. 2 illustrations.—ZDA.   19924

5.4.5

Moisture Permeability of Organic Coatings. M. Kronstein, J. Rivera, H. Abramski and F. Weber. Paint Varnish Products, **49**, No. 13, 33-38, 96 (1959).

Experiments and results are described in evidence of the hypothesis that, for non-reactive pigments, particle size and shape has considerable influence on "density" of paint films. Test included blistering, light transmittance, water vapor permeability and salt fog exposure. Vehicles were polyvinyl acetate and styrene/butadiene copolymer latices, an alkyd and a vinyl alkyd. Pigmentations were combinations of rutile TiO_2 with Mg silicate (I), platy mica, 325-mesh (II), micronized mica, "1000" mesh (III) and micronized mica "3000" mesh (IV), etc. In polyvinyl acetate latex paint experiments using (I) and (II) as extenders, increased (II) up to a certain point reduced blistering but thereafter blistering increased. In alkyd paint experiments using (I), (II), (III) and (IV) as extenders, mixtures of (II) and (III) were optimum for light transmittance and water permeability; "denser" films are considered to result from mixtures of a larger-size extender, e.g., (II) and (III), than with mixtures of two very small sizes, e.g. (III) and (IV).—RPI.   19941

5.9 Surface Treatment

5.9.4, 5.4.5, 6.3.19, 3.5.9

Pretreatment of Zinc Before Painting. K. S. Rajagopalan and P. L. Annamalai. J. Sci. & Ind. Res., **18B**, No. 11, 497-498 (1959).

Performance of chromate and phosphate treatments as bases for the painting of zinc at elevated temperatures has been investigated. It is shown that phosphate treatment, despite its inherently poorer corrosion-resistant properties, is a more satisfactory paint base at elevated temperatures.—RPI.   19916

5.9.4

Sealing Anodic Oxide Coatings. Pt. II. S. Wernick and R. Pinner. Electroplating, **12**, No. 11, 421-425, 433 (1959).

Various sealing baths are described and compared; good corrosion-resistance is imparted by $K_2Cr_2O_7$ sealing and Ni or Co acetates are suitable for dyed coatings. Optimum pH for water-sealing is 6-9, and steam sealing is accelerated at 15 lb/in². Analytical methods of control are described. 29 references.—MA.   20248

5.9.4, 2.3.7

Sealing Anodized Aluminum. J. M. Kape. Metal Ind., **95**, No. 6, 115-118 (1959).

Available methods for sealing and testing sealed anodized coatings are surveyed. It is recommended from tests described that sealing should be carried out either with steam at 100 C or boiling distilled water at pH 5.5-6.0. The effectiveness of sealing is impaired by Ca or Mg salts, $CuSO_4$, or CuF_2 in the supply water, and the use of acid water (pH 4.0), particularly H_2SO_4 or oxalic acid. Poorly sealed work can be improved to some extent by treatment in boiling water, but not in steam. A test solution is recommended which gives a quantity measure of the quality of sealing in a shorter time than conventional SO_2 humidity tests. 13 references.—MA.   19938

5.9.4, 5.3.4

A Chemical Treatment Against Corrosion of Galvanized Steel Produced in Continuous Lines. G. Odone and G. Milanese. Metal Finishing J., **5**, No. 54, 237-240 (1959) June.

Authors tested the efficacy of various passivating solutions against white rust. The galvanized material was stored in a

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warehouse where conditions were favorable to white rust formation. Certain treatments based on chromium trioxide and concentrated sulfuric acid have proved satisfactory. The addition of small quantities of wetting agents is highly recommended. Comparative tests were made with other solutions using salt spray fog tests, etc. 4 figures, 2 tables.—ZDA.   19861

5.9.4, 6.3.6
Siliconizing of Copper with Silicon Tetrachloride and Nitrogen. (In Japanese.) Kyuya Nagasaki and Masami Kaneko. J. Japan Inst. Metals (Nippon Kinzoku Gakkai-Si), **23**, No. 2, 113-116 (1959).

If copper is heated in a mixture of $SiCl_4$ vapour and nitrogen at 800 C neither thermal decomposition of $SiCl_4$ nor reaction between it and Cu takes place. However, when Si powder is added, siliconizing occurs at 600-800 C. It is thought that $SiCl_4$ acts as a Si carrier.—MA.   19862

5.9.2, 6.3.15
Descaling of Titanium and Its Alloys by the Molten Salt Bath Methods. (In Japanese.) Yasumoto Otake. Copper Works. Sumitomo Metals, **11**, 31-45 (1959) July.

Comparison of the molten caustic soda containing oxidizing agents with the sodium hydride method proved the latter superior. If optimum conditions are observed hydrogen absorption is small. Beta structure increases the absorption. —RML.   19873

5.9.4, 2.3.2
Chromate Treatment of Zinc and Other Metals. Part I. Accelerated Testing of Chromate Coatings. K. S. Rajagopalan and P. L. Annamalai. J. Sci. Ind. Research (India), **18A**, 171-175 (1959) April.

Results of some tests on Cronak treated zinc are compared and the value of various tests is assessed. It is concluded that chromate treatment gives satisfactory protection under conditions of high humidity and salt concentrations of up to 3% at temperatures below 35 C, but in the presence of salt a rise in temperature has an adverse effect and therefore chromate treatment is likely to fail in coastal tropical regions. It is recommended that users of chromate treatment also employ the A.R.E. or similar salt spray tests when assessing the value of proprietary formulations for protection at elevated temperatures. 4 figures, 3 tables.—ZDA.   19899

5.9.4, 6.4.2
Significance of Different Anodizing Processes for Aluminum and Its Alloys. J. M. Kape. Machinery (London), **95**, No. 2450, 855-859 (1959).

A 7-15% solution of H_2SO_4 is used commercially at 15-23° C, with c.d. of 6-24 amp/ft² of Al anode surface. The effects of variables are tabulated, and usages for the various coatings are briefly described. The properties of anodic finishes on various alloys are set out.—MA.   19798

5.9.2, 6.3.15, 3.2.2
Currently Available Processes for Pickling Titanium and Its Alloys. Metal Finishing J., **5**, No. 50, 55-58 (1959).

Precautions must be taken to avoid H embrittlement. Molten-salt processes such as the Na hydride, Virgo, and Kolene No. 4 processes are the fastest and safest methods, but plant outlay is high. For scale formed below 700 C

acid pickles are recommended.—MA.   19824

5.9.4, 6.4.2, 8.8.5, 5.3.4
Influence of the Structure of Aluminium Pressure Die-Castings on the Quality of Decorative Anodic and Cathodic Coatings. A. Buckeley. Aluminium, **35**, No. 10, 568-571 (1959).

Deals with the difficulties in obtaining satisfactory anodic coatings on the alloys used for pressure die-castings, but which are less noticeable in the case of electroplating. The main trouble is caused by unevenness in grain size due to bad metal distribution in the mould, which can, however, be partly overcome by heat-treatment at high temperature, provided the metal is pore-free.—MA. 20094

6. MATERIALS OF CONSTRUCTION

6.3 Non-Ferrous Metals and Alloys—Heavy

6.3.5, 3.7.2, 3.5.9, 3.8.4
Oxidation Characteristics of Columbium Alloys. Technical Report 467-5. Gerald Gordon, Coulson Scheuermann and R. Speiser. Ohio State Univ. March, 1959, 56 pp., Contract N6onr-22528. Available from Ohio State Univ. Research Foundation, Columbus, Ohio.

A survey of the available data pertaining to the niobates showed that in most cases the melting points are above 1200° C and are, therefore, not a fruitful basis for screening. The binary niobium-titanium system was investigated for oxidation resistance at 860°C. Alloys in this system, particularly one containing 48 at. % niobium, 52 at. % titanium, exhibited very good oxidation resistance at temperature, but spalled violently upon cooling. In an attempt to suppress spalling of the niobium-titanium alloys, chromium was added as a ternary addition. Chromium further increased the oxidation resistance but had little effect on the spalling behavior. Alloys containing chromium were brittle and difficult to fabricate. It was found that, at 1000°C, progressive additions of zirconium greater than 10 at.% to niobium decreased the oxidation rate and increased the protective nature of the oxide scale formed ($6ZrO_2$. Nb_2O_5). A minimum in the oxidation rate occurred at about 55 at. % zirconium. The oxide scale formed on an alloy containing 57 at.% zirconium was protective at 1000°C for times up to five hours and did not spall upon cooling. After five hours at 1000°C there is a rapid increase in the oxidation rate (break-away) which is associated with the formation of a bulky, porous oxide at the specimen edges. At 1100°C the oxidation rate follows a parabolic relationship for at least 17 hours at temperature. High zirconium alloys were found to undergo both internal and external oxidation. Titanium was added as a ternary addition in an attempt to decrease the oxidation rate and to suppress the rapid increase in weight gain which occurs after several hours in the niobium-zirconium alloys. One alloy 50 at.% Zr, 45 at.% Nb, 5 at.% Ti, was found to possess an excellent combination of low oxidation rate and protective, non-spalling oxide film. The oxidation behavior at 900 to 1000°C can best be described by a quartic relationship, $w^4 = kt$. This unusual relationship appears to result from the process of subscale formation. The subscale manifests itself as a lamellar dispersion of oxide phases. This dispersion may increase the high tempera-

ture strength while decreasing the available ductility. Chromium additions to the best niobium-zirconium alloys gave relatively good oxidation resistance at 1100 and 1200°C, but the breakaway phenomenon was observed after 10 hours at 1000°C in an alloy containing 45 at. % Nb, 45.7 at.% Zr, 9.3 at.% Cr. (auth). —NSA. 19843

6.3.15, 3.7.2, 3.5.9
Some Properties of Titanium-Aluminum-Base Ternary Alloys. (In Japanese.) Ichiji Obinata and Shigeo Aoki. J. Japan Inst. Metals (Nippon Kinzoku Gakkai-Si), **23**, No. 1, 55-59 (1959).

Resistance to deformation and oxidation of Ti alloys containing Al 1.16, 3.10, and 4.02%, Al 4.87 and Cu 1.59%, Al 5.21 and Si 0.41%, Al 5.31 and Sn 1.66% were investigated at 500-800 C. Al generally increased resistance to both deformation and oxidation of Ti, at 500-800 C. Ternary alloys, especially with Cu 1.59%, showed good resistance to deformation at 700-800 C and the Sn-containing alloy showed excellent-oxidation-resistance up to 700 C in dry air. The rate-of-oxidation curves at 800 C in dry air showed many abrupt changes during the first 10 hr. of the reaction, indicating a probable change in the rate-determining factors. Electron-diffraction analyses showed that the oxide film always contained TiO_2.—MA. 19865

6.3.9, 3.5.9
Effect of Testing Atmospheres on the Creep-Rupture Properties of Mo- base Alloys at 1800° F (980° C). Dean D. Lawthers and M. J. Manjoine. (Am. Inst. Mining Met. Engrs. Conf. on) High-Temp. Materials, 1957, **1959**, 486-497.

Creep strength and life of vacuum-sintered and arc-cast Mo alloys at 1800°

F are increased by testing in vacuo. By gradually raising the stress applied to specimens tested in an impure He atmosphere, the creep strength and life can be increased. Creep life is prolonged without loss of ductility by allowing a critical amount of air to diffuse into Mo. This is probably due to O or N reacting with Mo to form a second phase.—MA. 19799

6.3.10, 4.6.11, 3.5.8
Corrosion of Inconel by Sea Water. Progress Report V. M. J. McGoff and C. J. Glaser. MSA—Memo—138, Jan. 20, 1959, 15 pp. Available from MSA Research Corp., Callery, Penn. Contract NObs-77023.

Insulated and stressed 1 in. Sch 40 Inconel pipe specimens were periodically wetted with synthetic sea water and thermally sycled for 1 week over a temperature range of ~ 200 to 650 F. The specimens did not undergo chloride stress corrosion. The effect of heat treating and cold working on Inconel's susceptibility or resistance to chloride stress corrosion was not established since this form of corrosion did not occur in the short time allotted for the test. Although the Inconel pipe did not experience chloride stress corrosion, chemical corrosion of Inconel by sea water, in the form of pitting, did occur during a 5 week cycling period. (auth).—NSA. 19817

6.3.6, 2.3.6, 4.3.2, 5.8.1
Effect of Chlorine Ions on the Attack of Nitric Acid on Copper Single Crystals. Eginhart Biedermann. Z. Metallkunde, **50**, No. 8, 481-486 (1959).

When a single-crystal copper sphere is etched in 65% nitric acid, ripple patterns are produced if Cl^- ions, in amounts as small as $10^{-7} - 10^{-4}$, are present in the acid. The Cl^- inhibits dissolution of the copper; even as little as 0.003% reduces the rate of dissolution by 5%. Although the ripple patterns form round the cube poles of the crystal, they are unrelated to the crystal structure. The patterns are particularly noticeable at Cl^- concentration of 2-4×10^{-5}; their dimensions and the width: depth ratio depend on Cl^- concentration, time, and distance from the cube pole, and are predominantly a feature of the dynamic equilibrium between the dissolution of the copper by the nitric acid and the formation—and inhibiting effect—of films of absorbed Cl^- on the copper surfaces. —MA. 20072

6.3.20, 3.4.6, 3.5.9, 3.5.7
Post Breakaway Oxidation of Zirconium and Its Alloys. Tatsuo Maekawa and Takuya Hata. Nippon Kinzoku Gakkai-Si, **23**, No. 7, 385-388 (1959). (In Japanese.)

Post-Breakaway oxidation rate of reactor-grade pure Zr, Zr-2.5% Sn, and Zr-0.24% Fe in dry O and air were measured at 500-850 C and 15-760 mm Hg pressure. A high oxidation rate and high pressure-dependence were found for pure Zr and Zr-0.24% Fe oxidized in O. A low oxidation rate and low pressure-dependence were found for the oxidation of Zr-2.5% Sn in O and air. The oxidation rate and its pressure-dependence increase markedly with temperature for the oxidation of pure Zr and Zr-0.24% Fe in air. A relationship between oxidation rate and its pressure-dependence was established. 17 references.—MA. 20095

6.3.15, 3.7.3, 3.5.9
Properties and Heat Treatment of the Titanium Alloy TiAl7Mo4. (In German.)

W. Knorr. Tech. Mitt. Krupp, **17**, 111-123 (1959) Sept.

Properties of a titanium alloy containing 7% Al and 4% Mo were investigated. In the incandescent state, tensile strengths between 104 and 124 kp/mm² were found. The effect of deformation on the tensile strength and the effect of the deformation degree and the deformation temperature on the ductility are greater than the effect of a change of the alloy composition in the concentration range investigated. The tensile properties can be increased by heat treatment so that a good depth hardness can be obtained. The yield point, with increasing quenching temperature, passes through a minimum value at approximately 900 C which is apparent with the transformation of the mechanically stable beta phase. Favorable combinations of strength and ductility were obtained after quenching from 900 C and annealing at 550 C. The structural forms arising in the processing and from heat treatment and their relationship with the mechanical properties are described. The best properties at room temperatures have a polygonal $(\alpha + \beta)$ form which was obtained with final deformation at the lowest temperature possible. This fine-grained state possesses, however, relatively poor creep properties, but transformation yield improved values. Some time-state values at 400 and 500 C show a relatively high heat resistance for titanium alloys. The embrittlement observed at 500 C raises doubts as to the utilization of the alloy for extended use at temperatures over 400 C. (tr-auth)—NSA. 19971

6.3.6, 4.4.8, 3.8.4
Kinetics of the Dissolution of Copper in Aqueous Solutions of Aliphatic Amines. S. C. Sircar and D. R. Wiles. J. Electrochem. Soc. **107**, 164-167 (1960) March.

Studies of the rate of dissolution of copper in aqueous solutions of ammonia, and methyl-, ethyl-, and n-butylamines under a high pressure of oxygen have shown the reaction to occur in two stages: a rapid pre-equilibrium involving the free amine molecule, and a slower reaction step involving either the free amine molecule or its conjugate acid.— BTR. 20176

6.3.13, 3.4.6, 3.7.2
Investigation of the Properties of Tantalum and Its Alloys. Period covered May 1, 1958 through December 31, 1959. Frank F. Schmidt, William D. Klopp, William M. Albrecht, Frank C. Holden, Horace R. Ogden and Robert I. Jaffe. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., WADD-TR-59-13, Feb. 12, 1960, 162 pp. Available from Office of Technical Services, Washington, D. C.

Reactions of unalloyed tantalum with air, nitrogen, and oxygen were studied. Vacuum sintering of high-purity and high-impurity-content tantalum powders was investigated to determine the conditions required for purification. The effects of alloying on the oxidation behavior of tantalum were determined. Several alloying elements were found to be effective in reducing both scaling and contamination. Interstitials were studied for their effects on mechanical behavior at low and elevated temperatures. Screening studies were conducted on the effects of substitutional alloying on mechanical properties at room temperature and at 2200 F. References are included. (auth)—NSA. 20177

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The present production model is particularly suitable for the protection of well casings of moderate current requirements, extensive hot spots on bare gas pipe lines, and also for furnishing supplemental power for the protection of coated pipe lines and heater treaters or other salt water handling equipment, just to name a few of the potential applications for this commercially available unit.

CPS is the sole outlet for this jointly developed unit as applied to the cathodic protection field. Contact our main office in Houston or any of the below-listed branch offices for operating data and cost information.

6.3.20, 8.4.5

Zirconium Ingots Are Melted from Various Types of Zirconium Scrap. E. S. Foster and W. J. Hurford. Westinghouse Electric Corp, Atomic Power Div. U. S. Atomic Energy Commission Pubn., WAPD-RM-96, Nov. 13, 1951 (Declassified Feb. 16, 1960), 8 pp. Available from Office of Technical Services, Washington, D. C.

Experiments are described in which the problems encountered in melting and cleaning scrap zirconium were investigated. The ingots made in these experiments were evaluated to determine if

they were within the specification limits of hardness, corrosion resistance, and chemical composition for use in the Mark I core. Data and conclusions are included. —NSA.　　　　20171

6.3.10, 4.3.2, 4.4.2

Study on Corrision of a Sintered Alloy Consisting of 60% Ni, 20% Fe, and 20% Mo. (In German.) H. J. Booss, Arch Eisenhüttenw., **31**, 195-197 (1960) Mar.

Cold rolled sheets are treated with nitric, sulfuric, hydrochloric, citric, acetic, tartaric and hydrofluoric acid and the weight losses are measured according to acid-concentration and reaction time. Influence of acid treatment on tensile strength and elongation of annealed wires. Corrosion resistance of sheets under various conditions.—RML.　　20136

6.3.15, 8.4.5, 3.7.3, 3.7.2

Some Studies on the Uranium-Molybdenum Alloy. (In Japanese.) M. Kawasaki R. Nagasaki, M. Itagaki and T. Takemura. J. Atomic Energy Soc. Japan, **2**, 136-146 (1960) March.

U-Mo alloy is of interest as power-reactor fuel. The characteristic behavior of the alloy when subjected to certain heat treatments and its general properties were investigated. The specimens were made by vacuum induction melting and were rolled at 600 and 900 C. In the heat treatment tests, the phase changes by quenching from various high temperature phases, the effects of quenching rate from gamma phase range, and Ms temperature for 1.30% Mo alloy were studied. Thermal cycling test revealed that greater improvement was obtained by gamma quenching followed by alpha annealing for the rolled rods with molybdenum content ranging from 0.5 to 9.0%. Oxidation test in air at 300, 400, and 500 C had shown that the rate constant of oxidation decreased with increasing molybdenum contents in the lower molybdenum range, but it increased as molybdenum contents became higher. The same tendency was observed on the corrosion test in hot water. The minimum weight loss in 350 C hot water could be obtained at 12 wt.% molybdenum. (auth) —NSA.　　　　20021

6.3.15

Corrosion Constants of Alloys with Uranium Base. Pt. I. (In Dutch). M. J. Brabers. Atoomenergie, **2**, 1-7 (1960) Jan.

In this first part of the article the corrosion of unclad uranium alloys is investigated. The corrosion properties of U-Mo, U-Nb, U-Mo-Nb, other ternary alloys with a U-Mo base, and U-Si alloys were given. (tr-auth).—NSA.　　20028

6.3.5, 3.8.4

Oxidation of Niobium. B. B. Argent and B. Phelps. J. Inst. Metals, **88**, No. 7, 301-304 (1960) March.

Oxidation rates of pure niobium were measured in dry and moist oxygen and air over the range 400-1050 C. It is found that: (1) the form of the oxidation-rate/temperature curves for niobium is dependent on the specimen shape and dimensions; (2) niobium oxide in contact with niobium shows an anion-deficient lattice at temperatures near 700 C; (3) a cation-deficient lattice is formed in the region of 450 C, but it is suggested that this is an effect dependent on the formation of metastable oxides; and (4) the formation of non-stoichiometric oxides accelerates oxidation. Apparent anomalies in the oxidation rates can be explained by departures from stoichiometry in the oxides. (auth)— MA.　　　　20152

6.3.13, 4.3.2, 4.3.3, 4.4.1, 4.7

Corrosion Resistance of Tantalum, Applications in the Chemical Industry. F. G. Cox. Corrosion Technology, **7**, 69-74 (1960) March.

Corrosion of tantalum, niobium and niobium (91-5%)-tantalum (95-5)-niobium alloys to inorganic mineral acid, alkali, organic chemicals, molten metals and human body fluids. The temperature range is 20-500 C for liquids and gases, up to 1740 C for molten metals.—RML.　　　　20244

6.3.15

Corrosion Resistance of Titanium. A. C. Wood. Corrosion Technology, **7**, 135-138 (1960) May.

For most corrosion-resistant applications, commercially pure titanium is chosen in preference to titanium alloys. The alloys offer no advantage in corrosion resistance over the pure metal, which is easier to fabricate.—BTR.　　　　20242

6.3.20, 3.7.2, 8.4.5

Development of High-Strength Corrosion-Resistant Zirconium Alloys. John A. De Mastry, Frederic R. Shober and Ronald F. Dickerson. Battelle Memorial Inst. U. S. Atomic Energy Commission Publication, BMI-1418, Feb. 22, 1960, 19 pp. Available from Office of Technical Services (U. S. Department of Commerce, Washington, D. C.).

Approximately 100 ternary and quaternary sponge-zirconium alloys were screened for structural and cladding applications in a natural-uranium-fueled heavy-water-moderated power reactor. The alloy additions studied included 2 to 4 wt.% tin, 0.5 to 2 wt.% molybdenum, and 1 to 3 wt.% niobium. The effect of 0.1 wt.% iron and 0.05 wt.% nickel additions to the experimental alloys was evaluated. All compositions were arc melted, rolled at 850 C from a helium-atmosphere furnace, vacuum annealed 4 hrs. at 700 C, and furnace cooled. Room- and elevated-temperature hardness measurements were used to estimate the tensile strengths of the alloys, while corrosion resistance was evaluated by 1000-hr. exposures to static 300 C water. (auth)— NSA.　　　　20232

6.3.20, 3.7.2, 4.3.2

Higher Purity Boosts Zirconium Resistance. W. E. Kuhn, Carborundum Co. Chem. Eng., **67**, No. 3, 154, 156, 158, 160 (1960) Feb. 8.

Recently improved metallurgical techniques yield commercial grade Zr with low impurities with corrosion resistance superior to impure metal. Table of corrosion data in 20% HCl (boiling and 200 C) shows that small decrease in impurity content, as indicated by change to lower hardness values, produces remarkable decrease in corrosion rate, accompanied by change from intergranular pitting to uniform surface attack. Surface condition has important influence on corrosion behavior of Zr; graph shows breakaway corrosion associated with as-received and abraded surfaces. Electrolytic polishing and vacuum annealing eliminate breakaway corrosion. Sensitivity of Zr to Fe and Cu contamination of 20% HCl is considered. Another graph shows how corrosion weight loss is affected by changes in HCl concentration at various levels of temperature. Mention is also made of Zr behavior in H_2SO_4, HNO_3 and H_3PO_4. Fabrication problems and lining with Zr are discussed, and use of Zr in chemical equipment commented upon. 11 references.—INCO.　　　　19805

6.3.6, 4.6.6, 3.2.2, 3.6.6, 3.5.8

How temperature, Velocity of Potable Water Affects Corrosion of Copper and Copper Alloys. Part 2. What is Corrosion? M. F. Obrecht and L. L. Quill. Michigan State Univ. Heating, Piping and Air Conditioning, **32**, No. 3, 109-116 (1960) March.

As an introduction to subsequent articles on effects of various types of potable waters on copper and its alloys, a review of some types of corrosion and of corrosion theory is presented. Corrosion of nonferrous metals in aqueous solutions may be due to any one of following: direct chemical attack, pitting corrosion, galvanic corrosion, stress corrosion, corrosion fatigue, or erosion-corrosion or impingement corrosion. Oxidation states of Cu and calculation of cell potential in a system consisting of Cu and pure water are discussed. Polarization effects, and factors which affect overvoltage are considered. Discussion of some of factors which influence rate and type of galvanic corrosion covers effect of temperature, oxygen concentration, hydrogen ion concentration, and composition of solution. Photos illustrating different types of corrosion of Cu and Cu alloys are included.—INCO.   19866

6.3.20, 4.3.2, 3.5.9

Corrosion Resistance of Zirconium in Sulfuric Acid at Elevated Temperature. (In Japanese.) Kazuyoshi Okano, Yukinori Ota and Yoshiharu Kitamura. Corrosion Engineering, **9**, No. 3, 100-102 (1960) March.

Studies on purified zirconium in sulfuric acid solutions of 50, 60, 70, 80 and 90% at 95, 140, 185 and 200 C. No significant change was observed with concentrations of 50 to 70% but striking increase in corrosion was found with concentrations of more than 80%. At temperatures of 95 to 200 C, the relationship between corrosion rate and temperature was nearly linear on logarithmic chart. —JSPS.   19874

6.3.21, 3.7.4, 3.5.4, 3.7.2

Development of Thorium-Uranium-Base Fuel Alloys. Martin S. Farkas, Arthur A. Bauer and Ronald F. Dickerson. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn.,

BMI-1428, March 18, 1960, 30 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

Thorium-uranium alloys were studied with the aim of developing alloys with improved irradiation behavior by control of microstructure. The effect of thorium purity, melting technique, hot and cold working and heat treatment on microstructure was investigated. The most significant microstructural differences occurred as a result of casting technique. The arc-melted alloys exhibited the most nearly ideal structure, that of a homogeneous dispersion of small-diameter uranium particles in a thorium matrix. In addition, the rate of work hardening, recrystallization behavior, density, and hot hardness of thorium-uranium alloys were determined. As uranium content increases, the rate of work hardening increases. The recrystallization temperature of thorium was found to increase by over 100 C when uranium is present. Molybdenum, niobium, zirconium and zirconium in conjunction with niobium were added to thorium-uranium with the aim of increasing irradiation resistance by stablizing the gamma-uranium phase and/or improving the high-temperature strength of the alloy. It was found that small additions of molybdenum or niobium were effective in stabilizing the gamma-uranium phase, while zirconium was an effective hardener at temperatures up to 600 C. Zirconium additions to thorium-uranium alloys were effective in improving the 300 C water corrosion resistance of thorium by a factor of two. (auth)— NSA.   20272

6.3.20, 3.2.3

Study of Oxide Films and Scales on Zirconium Alloys. Otto Zmeskal and G. M. Adamson. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-59-9-1, September 1, 1959, 30 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

A study was made of the structure of the oxide films found on various zirconium alloys, primarily those with zirconium-niobium base compositions. With thick films, or scales, formed by oxidizing an alloy, it was possible to obtain

directly a densely packed orthohombic oxide, 6 $ZrO_2 \cdot Nb_2O_5$; the amount of which increased with increasing niobium content, oxidation temperature, and oxidation time. High temperatures were required for high percentages of the compound. With thin-film studies difficulties were encountered because of distorted structures in the oxides and growth on preferred planes of the base metal. The thin films were all predominantly monoclinic in nature, even those on alloys with appreciable niobium contents. (auth)— NSA.   20233

6.3.20, 3.7.2, 3.2.2, 8.4.5

Hydrogen Absorption by Nickel Enriched Zircaloy-2. W. Yeniscavich, R. A. Wolfe and R. M. Lieberman. Westinghouse Electric Corp. J. Nuclear Materials, **1**, No. 3 271-280 (1959) October.

Specimens of Zircaloy-2 with varying nickel contents were exposed to autoclave corrosion, and also simultaneous corrosion and reactor irradiation in hot water loop. Increasing nickel content of Zircaloy-2 from 0.05 to 0.75 caused gross increase in hydrogen absorptivity, which resulted in embrittlement and severe loss of mechanical strength. This increased hydrogen absorptivity appears to be unique effect of nickel, because Zircaloy-2 specimens with increased iron and copper contents did not duplicate this effect. Enriching of all specimens was done by diffusion bonding. Tables, graphs, photomicrographs, 9 references.— INCO.   20234

6.3.20, 1.3, 3.2.2

Hydrogen Pick-Up in Zirconium Alloys, A Review of data up to June 1, 1959. G. J. Biefer, L. M. Howe, A. Sawatsky and F. H. Krenz. Atomic Energy of Canada Ltd., Chalk River, Ontario, Canada. CRMet-849, September, 1959, 69 pp.

Fundamental properties of the Zr-H system are discussed and the distribution of the hydride phase in α-Zr are shown. The thermal diffusion and concentration diffusion of H in Zircaloy-2 discussed, and a set of curves is given which permits estimation of the hydrogen enrichment that may result from a thermal gradient. The damage to a surface oxide by hydriding and the effect of the oxide film on the absorption of H by Zr during furnace charging are considered. Experimental data on the pick-up of hydrogen by Zircaloy-2 and other Zr alloys published prior to May, 1959, are reviewed relative to the effects of radiation, water composition, and the alloying elements. Data on the effect of ZrH_2 on the mechanical properties of Zr and Zr alloys are reviewed. The pick-up of H in fuel sheaths and by Zircaloy-2 pressure tubes is predicted. The applicability of Zircaloy-2 to present reactor designs is evaluated. Curves are presented to show expected rates of hydriding.—NSA.   19919

6.3.20, 4.6.2, 3.7.2, 3.73

Corrosion Resistance of Zr-Nb and Zr-Nb-Sn Alloys in High-Temperature Water and Steam. S. B. Dalgaard. March, 1960, 25 pp. Available from Atomic Energy of Canada Ltd., Chalk River, Canada. (CRMet-911; AECL-993).

An alloy of reactor-grade sponge zirconium-2.5 wt.% niobium was exposed to water and steam at high temperature. The corrosion was twice that of Zircaloy-2 while hydrogen pickup was found to be equal to that of Zircaloy-2. Ternary additions of tin to this alloy in the

Materials Deterioration
in the Atmosphere

The Mechanism by Which Non-Ferrous Metals Corrode in the Atmosphere by P. M. Aziz and H. P. Godard, Aluminium Laboratories, Ltd., Kingston, Ont.

Mechanisms of Atmospheric Corrosion of Ferrous Metals by C. P. Larrabee, Applied Research Laboratory, U. S. Steel Corp., Monroeville, Pa.

Principles and Procedures Employed in the Design and Interpretation of Atmospheric Corrosion Tests by H. R. Copson, Research Laboratory, The International Nickel Co., Inc., Bayonne, N. J.

Deterioration of Materials in Polluted Atmospheres by J. E. Yocum, Bay Area Pollution Control District, San Francisco, Cal.

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range of 0.5 to 1.5 had no effect on the corrosion resistance in water at 315 C up to 100 days. At higher temperatures, tin increased ,the corrosion, the effect varying with temperature. Heat treatment of the alloys was shown to affect corrosion resistance. (auth)—NSA. 20257

6.3.20, 4.3.2, 3.8.3, 3.8.2
Difference Effect and Anodic Behavior of Zirconium Dissolving in Hydrofluoric Acid. M. E. Straumanis, W. J. James and W. C. Custead. J. Electrochem. Soc., **107**, 502-506 (1960) June.

Zirconium dissolving in hydrofluoric acid exhibited a postive difference effect of such an efficiency that the hydrogen volume developed by the internal polarization current was completely overbalanced by the effect. As with other metals the effect was independent of the concentration of the acid and was accompanied by a strong shift in potential of the Zr electrode toward noble values (passivation). Similar potential changes were also recorded in presence of salts or more noble metals while they were displaced by the Zr. Simultaneously, the rate of dissolution of Zr dropped (nearly to zero with Pt^{4+} additions). In the latter case the black hydride film on the surface disappeared and the Zr turned bright and shiny (passive Zr). A decrease in formation of the hydride film was observed in other cases of anodic polarization. The activity of Zr returned when the anodic current was cut off. As the effect of local currents due to anodic polarization is reduced to a minimum, the high rate of dissolution of Zr is explained by direct chemical action of Zr with molecular HF. (auth)—NSA. 19985

6.3.16, 3.5.9, 3.8.4
Research on the Oxidation Behavior of Tungsten. Quarterly Progress Report No. 4 for March 16, 1959 to June 30, 1959. Rudolph Speiser. Research Foundation, Ohio State Univ., Columbus, July 1, 1959. 85 pp. RF Project 831. Contract AF33 (616)-5721.

Experiments were conducted to determine the oxidation characteristics of commercially pure tungsten in the temperature range of 680 to 1100 C at partial pressures of oxygen from 0.05 to 0.21 atmosphere. The mechanism of oxidation of tungsten in air was found to occur by the diffusion of oxygen ions through the scale to the metal-oxide interface. Initially the kinetics of oxidation follow a parabolic rate law. This parabolic behavior is subsequently replaced by linear rate behavior. Three oxides were observed to play a part in the oxidation of tungsten. The first oxide, WO_2, was apparent only at low temperatures and for very short times. The second oxide is thought to be $W_{18}O_{49}$ or $W_{20}O_{58}$. This blue oxide, which appeared to be very dense and adherent, grew rapidly to a limiting thickness of approximately 10 microns. The third oxide, or outer oxide, was identified as WO_3. This oxide existed at all temperatures and was formed with a physically porous structure. A reduction in the partial pressure of oxygen decreases the linear and parabolic rate constants and increases the thickness of the blue oxide layer. The activation energies were calculated from rate constant data and were found to be 35.0 K cal in the parabolic range and 36.5 K cal in the linear range. The fact that the activation energies are approximately equal indicate that diffusion through the blue oxide layer is the controlling step in both processes. (auth)—NSA. 20187

6.3.20, 6.3.13, 8.4.5, 6.3.5
Rare Metals for Special Purposes. J. P. Denny and L. F. Kendall, Jr. Eng. Materials Design, **2**, No. 12, 624-627 (1959).

Zirconium is characterized by its outstanding resistance to attack by alkaline and acid media; commercial-grade zirconium, containing 1-2.5% hafnium, is used for most purposes, but in atomic reactors zirconium containing traces of tin, iron, nickel and/or chromium is employed. Hafnium has the properties of zirconium, plus unusually high absorption of thermal neutrons. The low thermal-neutron capture cross-section of niobium (1.2 barns), high d, and high strength at temperatures up to 1100 C render it suitable as a canning material for fuels in experimental reactors. Tantalum has high corrosion-resistance, and is used in industrial chemical apparatus and for implants in the human body. Chromium and vanadium are used mainly as alloy elements, and rhenium in electron tubes and for electrical contacts. Physical and mechanical properties are tabulated.—MA. 20255

6.3.20, 3.7.2, 4.6.2
Constitution of Zirconium-Palladium Alloys. (In German.) Kurt Anderko. Z. Metallkunde, **50**, 681-686 (1959) Dec.

Small additions of palladium increase the corrosion resistance of arc-melted sponge zirconium in pressurized water and steam. The phase diagram of the zirconium-palladium system was established in the range 0 to 50 at.% palladium by means of thermal, microscopic, resistometric, and roentgenographic analysis and was investigated in a cursory manner in the range 50 to100 at.% palladium. The following intermediate phases were observed: Zr_2Pd, $ZrPd$, $ZrPd_2$, and $ZrPd_3$. The solubility of palladium in α-zirconium lies below 0.1 at.%, that in β-zirconium amounts to 11.5 at.%. The metastable α phase occurs as a transition phase in the decomposition of the β-zirconium phase. (auth)—NSA. 20246

6.3.17, 4.6.1, 5.3.4
Corrosion of Unalloyed Uranium by Water Including a Consideration of Protective Coatings. B. E. Hopkinson. Corrosion Technology, **6**, No. 11, 337-340 (1959) Nov.

Summarizes available information on corrosion of unalloyed U, a possible fuel for some types of water-cooled reactors. Protective coatings are also considered, since mechanical barrier is only known means by which unalloyed U may be protected from attack by high-temperature water. Effects of temperature variations of water, and of dissolved gases (O_2, H_2), solids and liquids (inhibitors, H_2O_2, KCl, KOH and Na dichromate) are reviewed. Influence of heat treatment of U and of purity of metal is dealt with. Corrosion resistance of numerous coating laid down by 3 main techniques —electroplating, diffusion coating, and production of protective oxide and nitride film—is covered. Electroplated coatings include Ni, Ni-Mo and Kanigen Ni. Diffusion coatings are considered under 3 types: solid-solid reactions (including Cb layer on Ni-plated U), solid-liquid reactions (including all hot-dipping and metal spraying), and solid-gas reactions (decomposition of metallic halide and evaporated metal coats). Mechanism for U-water reaction involves H_2 in some way and effect of H_2 is usually considered deleterious to corrosion resistance. Tables, 39 references. —INCO. 19845

6.3.10, 3.7.4, 3.2.2

Phenomena of Intergranular Adsorption and Their Relation to Intergranular Brittleness of Nickel. (In French.) G. Henry, J. Plateau, X. Wache, M. Gerber, I. Behar and C. Crussard. Compt. Rend. **248**, 1510-1512 (1959) March 9; Mém. sci. Rev. Mét., **56**, No. 4 417-426 (1959).

Intergranular brittleness of commercially pure Ni is caused by heating at, or slow cooling through, temperature <800 C and is associated with striae at the grain boundaries analogous to those appearing in superficial high-temperature oxidation of metals under reduced 0 pressure. It is suggested that 0 present as impurity in solid soln, adsorbs at the grain boundaries, resulting in a decrease of interfacial energy and, hence, brittle fracture.—MA.   19855

6.3.15, 4.7, 3.2.3

Nature and Growth of Interaction Layers Formed During the Reaction Between Solid Titanium and Liquid Aluminum. J. Mackowiak and L. L. Shreir. J. Less-Common Metals, **1**, No. 6, 456-466 (1959) Dec.

During the interaction of solid Ti and liquid Al, the interacting layers were observed to develop an unusual cruciform pattern. The constituents of the layers were identified as Al and TiAl₃ by microhardness, metallographic and X-ray techniques.—BTR.   19896

6.3.17, 4.3.2

Dissolution of Uranium Metal and Its Alloys. Robert P. Larsen. Analytical Chem., **31**, No. 4, 545-549 (1959).

Reactions of common acids, HCl-ethyl acetate, and Br-ethyl acetate with U and its alloys were studied, and recommended procedures for dissoln, are given. 10 references.—MA.   19788

6.3.11, 3.7.1, 3.8.4

Studies on the Platinum-Rich Alloys in the System Platinum-Molybdenum. (In Japanese.) Hideo Nishimura and Hirozo Kinura. J. Japan Inst. Metals (Nippon Kinzoku Gakkai-Si), **23**, No. 10, 616-620 (1959).

Physical and technical properties of Pt-Mo alloys were studied. The maximum solubility limit of Mo in α-phase (Pt-phase) is 15% and the lattice parameter of α-phase alloys containing increase in Mo. Cold-working can be applied to α-phase alloys containing < 6% Mo, and their annealing temperature is above 1100 C. At high temperature, i.e. above 1000 C, MoO₃ volatilizes as rapidly as it is formed, and the β-phase transforms into α-phase by oxidation in air. A preferred oxidation of Mo in α-phase was observed on prolonged heating in air, and proceeded according to a log.-rate law.—MA. 19918

6.3.15, 3.8.4

System Titanium-Zirconium-Oxygen. Michael Hoch, Robert L. Dean and others. Cincinnati University. U. S. Wright Air Development Center, Technical Rept 59-539, July, 1959, 83 pp. Available from Office of Technical Services, Washington, D. C. (Order PB 161435).

General shape of the 1450 C isotherm of the Ti-TiO-ZrO₂-Zr region was calculated from the surrounding binary phase diagrams. The phase boundaries were accurately determined by investigating 50 compositions using X-ray and metallographic techniques. The isotherm at 1500 C for the region TiO-TiO₂-ZrO₂ was obtained by investigating 45 compo-

sitions, using X-ray diffraction. The activities of titanium and Tio in the α + TiO + tetragonal ZrO₂ and the two α + β + tetragonal ZrO₂ regions were measured using the Knudsen effusion method. The solidus and liquidus surfaces were determined by observing samples suspended with a fine tungsten wire in a tungsten crucible, and heated in vacuum. The oxidation of titanium-zirconium alloys was also investigated. The presence of zirconium in titanium, and vice versa, decreases the oxidation resistance and the alloys oxidize faster than the pure metals.—GRR.   19909

6.3.11

Metals and Alloys of the Platinum Group. (In English.) Ernst Raub. J. Less-Common Metals, **1**, No. 1, 3-18 (1959).

The six platinum metals may react rapidly at elevated temperatures with refractory materials under reducing conditions, while the reaction between oxygen and the platinum metals and their alloys is also discussed. The techniques employed in the manufacture of alloys are described and the structure of the binary alloys of the platinum metals with one another and with other high-m.p. metals is considered. An unbroken series of solid solutions was formed at high temperatures in the alloys of the four f.c.c. platinum metals with each other, but at low temperatures miscibility gaps were found in some alloys. It was difficult to prove the existence of these in all alloys owing to the slow approach to equilibrium. Alloys of platinum metals with one h.c.p. component, manganese, and with metals of Groups IVA, VA, and VIA are considered together with alloys of the f.c.c. platinum metals with the f.c.c phases of iron, cobalt and nickel. 35 references.—MA. 19911

6.3.11, 8.4.5

Development and Properties of Silver-Base Alloys as Control Rod Materials for Pressurized Water Reactors. I. Cohen. Westinghouse Electric Corp. U. S. Atomic Energy Commission Pubn., WAPD-214, Dec., 1959, 122 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

Metallurgical design and properties of silver-base alloys which show considerable promise of fulfilling metallurgy, physics, and mechanical design requirements of control rods for nuclear pressurized water reactor plant service are described By extension of the Hume-Rothery electron concentration rule, ternary and quaternary Ag-base alloys were designed for metallurgical stability, and their physics worth, corrosion and physical and mechanical properties were determined. Of particular interest is the Ag + 15 wt.% In + 5 wt.% Cd alloy which is comparable to hafnium in neutron absorption characteristics. (auth)— NSA.   20293

6.3.4

Use of the Magneto-Mechanical Effect for (Cobalt-Nickel) Alloys of High Damping Capacity and High Strength. Alexander Cochardt. Z. Metallkunde,-50, No. 4, 203-206 (1959) April.

Unusually high damping capacity of the current chromium alloy steel—Cr 12, Ni 0.5, and C 0.1%—used for steam-turbine blades is attributable to magneto-mechanical hysteresis. The walls between the ferromagnetic domains of the material move backwards and forwards when the blade vibrates, this process consuming the vibrational energy of the

blade and causing its high damping capacity. Examination of 55 binary and ternary alloys, based on Fe, Cr, Ni and Co to find an even better material led to the development of "NIVCO," a Co-base alloy containing 35% Ni and small amounts of other elements. Its properties at 650 C are similar to those of the current material at 500 C; it has a high irreversible magnetostriction, with excellent hardness and oxidation-resistance; its matrix has a f.c.c. structure; it is ferromagnetic up to at least 800 C. 14 references.—MA.   20294

6.4 Non-Ferrous Metals and Alloys—Light

6.4.2, 5.9.4, 4.3.3
Corrosion of Aluminum Treated by the Modified Bauer-Vogel Process in an Alkyline Medium. (In Hungarian.) Palma Szeki and Zoltanne Eollos. Kohaszati Lapok, **93**, 38-40 (1960) Jan.

Samples were oxide coated by the above process and treated subsequently in steam. The corrosion resistance was tested by exposing to the action of 8.1 to 9.9 pH caustic soda solutions. Samples that were oxide coated in a 1 pH solution showed the best corrosion resistance.—RML.   19934

6.4.2, 3.5.9
Mechanism of Attack of Aluminum-Iron-Nickel Alloys in Water Vapor Above the Critical Temperature. (In French.) P. LeLong J. Moisan and J. Hérenguel. Compt. Rend., **250**, 340-342 (1960) Jan. 11.

Selective corrosion at 440° C. and under 170 kg. per sq. cm. pressure between solid solution and eutectic in 1% Fe-1% Ni Al alloy. This type of "interphase" corrosion occurs in both as-cast and work-hardened alloy, is violent, and leads to total destruction of specimens. 4 references.—RML.   19777

6.4.2, 8.4.3, 7.4.1
Aluminum Bundles Will Work in Petroleum Service. R. I. Hildebrand. Sinclair Refining Co. Paper before American Petroleum Institute Refining Division, Detroit, May 9, 1960. Petroleum

Refiner, **39**, No. 5, 143-150 (1960) May.

Presents 18 case histories in 45 plants which show that aluminum exchangers and condenser tubes are superior to brass, steel or alloys in certain locations. Aluminum is recommended for fluid units (low chloride concentrations, OH condensers operating below 300 F); H₂S removal equipment, amine stripper OH condensers, amine exchangers, and amine coolers; H₂S-NH₃ stripper OH condensers, methylethyl ketone plants; light hydrocarbon and petrochemical plants; and low-temperature service. Aluminum should not be used where HCl and chloride salts, caustics and heavy metals are present, and should be avoided in couplings which cause galvanic action. Photos show failures in aluminum due to salt deposits and pitting.INCO. 19931

6.4.2, 8.4.3, 1.2.2, 7.6.1
Aluminum Use in Refineries is Increasing. (In German.) P. W. Sherwood, Werkstoffe u. Korrosion, **11**, No. 5, 265-269 (1960) May.

Acceptance of aluminum in petroleum refinery construction is growing rapidly. Main reason for this development is the excellent resistance of aluminum to corrosion in situations frequently encountered in refinery practice. Other reasons for the metal's growing popularity are found in its low unit weight, lost cost per unit volume and various secondary physical properties. A survey is provided of the corrosion behavior of aluminum in refinery processes and information is given on the composition and forms of aluminum alloys which are of primary importance in petroleum processing service. Comparative economics of aluminum and carbon steel are provided for some typical refinery applications and various successful areas for the use of aluminum-built process equipment are reported from actual commercial practice.   19969

6.4.2, 2.2.7, 4.6.7, 4.6.11
Corrosion Behavior of Aluminum Alloys Used in Shipbuilding. Part 1. (In Hungarian.) Zoltan Buray and Andras Domony. Kohaszati Lapok, **93**, 7-11 (1960) Jan.

Aluminum-copper-magnesium, aluminum-magnesium-silicon, aluminum-magnesium, aluminum-manganese and aluminum-copper-nickel alloys are exposed to the attack of fresh water and sea water from 0.90 days and then bend tested. Strain corrosion; corrosion behavior of welded assemblies.—RML.   20102

6.4.2, 3.5.9, 4.6.1, 8.4.5
Effect of Heat Flux on the Corrosion of Aluminum by Water. Pt. I. Experimental Equipment and Preliminary Test Results. J. C. Griess, H. C. Savage, T. H. Mauney and J. L. English. Oak Ridge National Lab., U. S. Atomic Energy Commission Pubn., ORNL-2939, May 13, 1960, 46 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

An experiment was performed to determine the effect of heat flux on the corrosion of 1100 aluminum by water under conditions simulating those that will exist in the High Flux Isotope Reactor. An a-c current was used to heat the test specimen, and a flow of water from a bypass line of a pump loop provided cooling. Water flowing at 33 ft/sec entered a coolant channel in the specimen at 155 F and was heated to 192 F on passing through the specimen. Heat fluxes of 0.50×10^6 and 1.62×10^6 Btu/hr • ft² on different parts of the specimen were constant during the 10-day test. The formation of adherent corrosion products on the coolant surfaces resulted in increasing aluminum temperatures as the test progressed. During the 10-day test the maximum temperature increase occurred at the coolant outlet and amounted to 189 F. In this region an adherent, nearly transparent, corrosion-product layer about 0.002 in. thick formed; the aluminum was penetrated to a depth of 0.007 in., 0.005 in. of which was intergranular in nature. The results of the test indicate that the temperature of the aluminum cladding on the fuel elements of the High-Flux Isotope Reactor will be higher than calculated, assuming clean aluminum surfaces, and that the extent of corrosion must be reduced either by the addition

of inhibitors to the water or by the use of an alloy more corrosion resistant than 1100 aluminum. (auth)—NSA.   20092

6.4.3, 3.4.6, 2.3.9
Oxidation of Beryllium in Carbon Dioxide and in Carbon Monoxide. S. J. Gregg, R. J. Hussey and W. B. Jepson. Nature, **186**, 468-469 (1960) May 7.

Oxidative behavior of beryllium at temperatures in the range 500 to 750 C in carbon dioxide, carbon monoxide, and mixtures of these two gases was investigated with the aid of a tracer technique using C^{14} labeled carbon dioxide. Results are presented graphically.—NSA. 20107

6.4.2, 8.4.5, 3.5.9, 4.6.1
Summary of Corrosion Investigations on High-Temperature Aluminum Alloys. Period covered Feb., 1955-October, 1956. C. R. Breden and N. R. Grant. Argonne National Lab. U. S. Atomic Energy Commission Publication, ANL-5546, Feb., 1960, 70 pp. Available from Office of Technical Services, Washington, D. C.

Tests were performed on aluminum alloys to evaluate their behavior in high-temperature, high-pressure, water-cooled and - moderated nuclear reactor environments. Test equipment, sample preparation, and test procedure are discussed. Aluminum-nickel alloys were found resistant to disintegration for periods up to 60 days in dynamic water at 600 F. The corrosion rates of the Al alloys M-388 and X-2219 at 600 F were found to be too high to merit consideration for cladding materials. The influence of pH, gas content, and velocity of the water on the corrosion of the above alloys was evaluated. Hydrogen addition at startup appeared to increase the degree of corrosion attack on the M-388 alloy. Irradiation tests on aluminum-nickel alloys revealed that the corrosion rate increased with distance from core. In-reactor samples of M-388 exhibited less corrosion attacks than out-of-reactor samples. Boiling water corrosion tests were performed on M-388 for 1612 hrs at 422 F with an average heat flux of 25,000 Btu per hr-ft.² The over-all cor-

rosion rate was 2.9 mil/yr. It is concluded that the corrosion rate of M-388 is acceptable for the specified test conditions: (1) absence of radiation; (2) demineralized water at 422 F; and (3) heat transfer rates not exceeding 40,000 Btu/ft.² No accelerated corrosion attack due to boiling heat transfer and no significant buildup of corrosion products on heat transfer surfaces were noted. Accelerated corrosion of M-388 was noted when coupled with Type 304 stainless steel and exposed to tap water at room temperature, or air-saturated, demineralized water at 680 F. A technique for stripping corrosion films from aluminum and aluminum-nickel alloys is given. —NSA.   20154

8. INDUSTRIES

8.4 Group 4

8.4.5, 6.4.1, 6.3.10, 6.2.5, 6.3.20
Problems of the Corrosion of Heterogeneous Nuclear Reactors. Vladimir Cihal and Ivan Sekerka. Hutnické Listy, **14**, No. 11, 978-983 (1959). (In Czech.)

Corrosion problems in such reactors cooled with CO_2 and water are reviewed. The most commonly used structural materials for CO_2 media are magnesium and beryllium alloys and alloy steels, while Al-, Ni- and Zr-base alloys and austenitic stainless steels should be used for water. 36 references.—MA.   20289

8.4.5, 1.2.5
AEC Safety Monograph. Chapter 11. Metal-Water Reactions. W. L. Brooks and H. Soodak, Editors. Nuclear Development Corp. of America. U. S. Atomic Energy Commission Pubn., NDA-15K-3, 1956 (Declassified December 29, 1959), 21 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

Reactions of reactor materials or coolants with water are considered. Aspects such as the reaction heat quantity, rate of reaction, self-sustaining characteristics of the reaction, and the quantity of hydrogen produced are evaluated. The most dangerous reactions are discussed, and results of in-pile tests of various metals are included.—NSA. 20212

8.4.5, 6.4.2, 6.2.5
Swimming Pool Reactors of 1000 KW, Melusine and Triton. Pt. V. Corrosion Problems in the Swimming Pool Reactors. H. Coriou. Bull. inform. sci. et tech. (Paris), No. 35, 47-52 (1959) Dec.

As aluminum is used for cladding the fuel elements, which are composed of an aluminum-uranium alloy, in the Melusine and Triton Reactors, the corrosion characteristics of aluminum are of importance. A brief survey is made of these characteristics and of the problems likely to be encountered in the operation of the Melusine and Triton. Corrosion of the stainless steel and the fuel is briefly mentioned.—NSA.   20216

8.4.5, 3.5.4, 6.3.10
A Fluoride Fuel In-Pile Loop Experiment. O. Sisman, W. E. Brundage and W. W. Parkinson. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-1965, Jan. 29, 1957 (Declassified March 6, 1959), 56 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

An Inconel loop circulating fluoride fuel (62½ mole % NaF, 12½ mole % ZrF₄, 25 mole % UF₄, 93% enriched)

was operated at 1485 F with a temperature of difference of about 35 F in the Low-Intensity Test Reactor for 645 hr. For 475 hr. of this time the reactor was at full power, and fission power generation in the loop was 2.7 kw, with a maximum power density of 0.4 kw/cc. The total volume of fuel was 1290 cc (5.0 kg), and the flow through the irradiated section was 8.6 fps (Reynolds number 5500). The loop has been disassembled and has been examined by chemical and metallographic analyses. No acceleration of corrosion or decomposition of fuel by irradiation was noted, although deposition of fission-product ruthenium was observed. No mass transfer of Inconel was found, and the corrosive attack was general and relatively light. The average corrosive penetration, in the usual form of subsurface voids, was 0.5 mil; the maximum penetration was 2 to 3 mils. (auth.)—NSA.   20179

8.4.5, 3.2.2
Corrosion Effects of a Turco 4306-B Simulated Flush on a 1706-KE Mock-Up Tube. T. V. Lane. General Electric Co. U. S. Atomic Energy Commission Pubn., HW-55854, April 28, 1958, 4 pp. Available from Office of Technical Services, Washington, D. C.

An out-of-reactor test in a mock-up tube with 25 Al clad dummies and with a Turco 4306-B flush is described. At 120° the flush causes no excessive corrosion (0.04 mil), but the corrosion rate was accelerated for 15 days following the flush resulting in a net over-all penetration of 0.1 mil. No unusual pitting of tube or dummies was revealed by microscopic examination. Trapping of Turco in stagnant crevices does not seem to be a problem.—NSA.   19836

8.4.5, 1.2.5
Chemical Decontamination for Tube Replacement. Harry F. Jensen, General Electric Company, Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-58208, Nov. 17, 1958, 5 pp. Available from Office of Technical Services, Washington, D. C.

In a production test at the Hanford Dual Purpose Reactor, it was found that considerable benefits can be obtained by decontamination with Turco 4306-B. The procedures for use in such decontamination are presented, and recommendations for their use as a tool for reduction of contamination effects are made. It is pointed out that sizeable percentages of total personnel exposure occur during tube replacement outages. Equipment and costs are also discussed as well as corrosion by Turco and waste disposal.—NSA.   19781

8.4.5, 4.7
Liquid Metal Fuel Reactor Experiment—Investigation of Precleaning and Decontamination Methods. W. S. Leedy. Babcock and Wilcox Co. U. S. Atomic Energy Commission Pubn., BAW-1094, February, 1960, 37 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

In the Experimental Liquid Metal Fuel Reactor (LMFRE), the steel surface exposed to the fuel solution must be cleaned prior to service, and radioactive contaminants must be removed from the system after service. To determine effective procedures, Croloy 2¼ specimens containing an artificially induced oxide scale were treated with various solvents, after which the corro-

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sion rates were determined. In addition, bismuth solubility in various solvents was determined, and fission product and corrosion product solubility was investigated. (auth.)—NSA. 19999

8.4.5, 8.10.2, 3.5.4, 6.4.4, 6.3.15
Metallurgy and Atomic Energy—Difficulty and Results Acquired. (In French.) M. Salesse. Nukleonik, **2**, 79-83 (1960) April.

As is known, the French atomic program is based in part on reactors cooled with gas and utilizing different moderators such as graphite, heavy water, and beryllium oxide. The tables presented survey the metallurgy situation with respect to reactors. The selection of a magnesium alloy for cladding, behavior of fritted beryllium oxide under the effect of radiation and corrosive conditions, and the radiation stability of uranium under high burn-up are the topics considered.—NS. 19973

8.4.5, 7.1
Considerations in the Design of a Nuclear Rocket. John J. Newgard and Myron M. Levy. Thiokol Chemical Corp. Nuclear Sci. and Eng., **7**, 377-386 (1960) April.

Design of a prototype nuclear rocket is described. For practical systems using uranium-loaded graphite for fuel elements within a graphitic core structure, and hydrogen as core coolant and propellant, it is possible to achieve specific impulses of at least 800 sec. The follow-

ing items are discussed: (1) design of the reactor core, reflector, and nuclear controls for a prototype design; (2) nuclear, heat transfer, and fluid flow considerations for typical design; and (3) reactor pertubations caused by fuel element ejection, corrosion-erosion, and hydrogen density changes. Some radiation hazards are considered. Nonreactor aspects of the rocket such as hydrogen handling and the coupling of the reactor to the rocket system are indicated. (auth.)—NSA. 19923

8.4.5
OMRE. Operating History and Experience. K. H. Campbell. Atomic International Div., North American Aviation, Inc. Nuclear Eng., **5**, 53-57 (1960) Feb.

An account is given of the operating history and experience gained from September 1957 to August 1959. At the time of the August 1959 shutdown, the reactor had accumulated a total of 1,400 Mwd of operation, 958 Mwd on the first core loading and 442 on the second. The decomposition rates of the organic coolant were calculated from total energy absorbed. Three fuel elements were removed for detailed inspection of heat transfer surfaces. The first two elements were removed after 549 and 958 Mwd at a nominal temperature of 750 F. The third element was removed from the second core loading after 442 Mwd of operation at temperatures slightly greater than 800 F. Mechanical and corrosion

test specimens were exposed to measured integrated neutron fluxes of the order of 9.0×10^{19} nvt thermal and 2.8×10^{20} nvt fast. The corrosion studies on out-of-pile specimens from the by-pass line were compared in the in-pile test specimens. The experience gained from the two years in which the OMRE was operational can be evaluated with some confidence with respect to the originally conceived economic and operating advantages inherent in the concept.—NSA. 20241

8.4.5, 6.6.4, 4.3.5
Preliminary Evaluation of Chlorine for Use as a Gas Cooled Reactor Safeguard. R. E. Dahl. General Electric Co., Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-63902 (Rev.), March 8, 1960, 19 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

An evaluation of chlorine in a high-temperature gas-cooled graphite-moderated reactor as a safeguard to control a runaway oxidation reaction was made. Experiments were performed which demonstrated the ability of a small amount of chlorine in an air stream to reduce the oxidation rate of graphite. Chlorine appeared to inhibit graphite oxidation by blocking active sites on the surface. On the basis of this mechanism, a rate law was derived which was consistent with observed behavior. —NSA. 20193

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Comparison of Corrosion Resistance of Basic Oxygen and Open Hearth Steel—Topic of the Month, by R. C. Talbot, R. N. Hobbs and W. A. Szymanski

Corrosion of Metals in Tropical Environments —Part 5: Stainless Steels, by A. L. Alexander, C. R. Southwell and B. W. Forgeson

A method for Prevention of Hydrogen Embrittlement of Tantalum in Aqueous Media,

by Claude R. Bishop and Milton Stern

Corrosion of Lead Cable Sheath, by K. G. Compton

Use of Pipe-To-Soil Potential in Analyzing Underground Corrosion Problems, by B. Husock

Oxidation of Iron-Chromium Alloys, by D. Lai, R. J. Borg, M. J. Brabers, J. D. MacKensie and C. E. Birchenall

A New Coating Material for Corrosion Control, by B. H. Mahlman and E. J. Kaatz

Use of Differential Thermal Analysis in Exploring Temperature Limits of Oil-Ash Corrosion, by Norman D. Phillips and Charles L. Wagoner

Microbiological Corrosion in Waterfloods, by J. M. Sharpley

Topic of the Month

Effect of Sunlight On the Corrosion of Steel*

By LEONARD C. ROWE*

Introduction

THE LITERATURE contains several reported experiences concerning the effect of ultraviolet or other light on metal corrosion. Light is not normally taken into consideration in corrosion studies because other factors are much more significant. But it has been proven that sunlight has an effect on the degradation of paint and certain other materials, and this factor is considered in their evaluation. Perhaps the effect of light on metal corrosion should receive more consideration than it has, particularly when there are differences in the amount or type of light striking a surface.

Laboratory Tests

The effect of sunlight on steel corrosion was first observed during some simple laboratory experiments. Mild steel specimens were placed in a petri dish, containing a 30 ml volume of distilled water. Each dish was covered with either clear or colored cellophane and exposed to sunlight. After a five-day test, the weight loss of steel under a blue filter was double that under any of the other filters. In six and one-half days, it was three times greater than that under a red filter.

Tests were repeated using only the red and blue filters. No significant difference in corrosion rate occurred over a ten-day test period. It was soon realized that water had been lost by evaporation during the first test but not during the last because of a tighter seal. This implied that the effect of variable light transmission may only be a factor when a thin

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TABLE 1—The Effect of Water Level on the Corrosion of Steel Under Filtered Sunlight

Volume of Water, ml	Corrosion Rate, mdd	
	Blue Filter	Red Filter
5	3.8	3.0
15	28.3	21.1
30	6.8	7.0

Abstract

Laboratory tests were made which showed that the corrosion rate of steel is greater under a blue filter than under a red filter in the presence of sunlight, provided that a thin film of water covers the metal surfaces. Outdoor tests of four-months duration verified the laboratory results. Steel specimens were exposed under molded glass filters which transmitted radiation within specific spectral regions. The results indicate that ultraviolet light activates the metal surface so that corrosion is initiated sooner or progresses at a faster rate than it would in its absence. Infrared light affects the metal surface so that subsequent exposure to ultra-violet light does not produce the same increase in corrosion.

3.5.4, 6.2.3

film of moisture covers the metal surface. The test was repeated with a variation in the volume of water added to each container. Using a 5-ml volume of water, the metal surface was not wetted; using a 15-ml volume of water, a thin film covered the surface. Coverage to a depth of one-eighth inch was obtained using a 30-ml volume of water. The temperature did not vary significantly between individual tests during the experiment.

The results of this experiment are shown in Table 1. The least corrosion occurred using the small volume of water, although the corrosion rate under the blue filter was 29 percent greater than that under the red filter. When a thin film of water covered the specimens, the corrosion rate was much more rapid in both cases, but was 34 percent greater under the blue filter than under the red filter. Similar results have been obtained with repeated experiments.

Outdoor Tests

In order to repeat these experiments under outdoor exposure conditions, a box-like specimen holder was designed for this purpose. The top of the box contained a molded glass filter, 6½ inches square, which transmitted the greatest percentage of radiation within a specific spectral region. Two specimens were mounted in each box in such a way that air entering from the openings in the side of the box freely circulated about the specimens, and direct sunlight had to pass through the filter before impinging on the metal surface. Specimens were shielded from direct contact with rain.

The holders were mounted on outdoor racks at a 45 degree angle, facing south. Some specimens were pre-exposed for one-half hour under ultraviolet or infrared light before exposing them outdoors under clear glass.

Specimens under infrared transmitting filters showed about 50 percent less corrosion after the first month than those under the other filters. The results after four months of exposure in the summer are shown in Table 2. There is good agreement between the corrosion rate obtained under the blue filter and that obtained when the steel was pre-exposed to ultraviolet light. A similar correspondence is noted in the corrosion rate obtained under one of the infrared transmitting filters and that obtained by pre-exposing specimens to infrared light. The corrosion rate is about 25 percent greater under ultraviolet light than under

TABLE 2—Four-Month Outdoor Exposure of Steel Under Filtered Sunlight

Filter	Light Transmission			Corrosion Rate, mdd
	Ultraviolet	Visible	Infrared	
Dark Blue	X	Below 520 mµ	..	6.2
Clear Corex D	X	X	X	5.9
Dark Red	..	..	X	5.6
Red Shade Yellow	..	Sharp cut-off	X	5.0
Clear Corex D¹	X	X	X	6.3
Clear Corex D²	X	X	X	5.0

¹ Pre-exposed for one-half hour to ultraviolet light.
² Pre-exposed for one-half hour to infrared light.

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infrared light. A substantial difference in corrosion rate was found between duplicate specimens in all cases. Specimens on the east side of the box always corroded at a faster rate than those on the west side. This is presumed to be due to some variation in exposure conditions rather than an effect from light.

Conclusions

These results show that the corrosion of steel can be affected by the type of light which strikes the metal surface. The high-energy, ultraviolet light produces an effect at the metal surface which leads to higher corrosion rates than in its absence. A radiation consisting of both visible and infrared light apparently results in less corrosion than infrared light alone. The results obtained by the pre-exposure of steel to either ultraviolet or infrared light clearly indicate that an initial surface reaction can occur which will affect future corrosion reactions. It is presumed that ultraviolet light activates the metal surface so corrosion is initiated either sooner or at a faster rate. The scope of this experiment was not sufficient to establish the difference between initial effects and a continued corrosion rate. If ultraviolet light affects the continued corrosion rate, it is difficult to understand how a pre-exposure to infrared light can have any effect on future exposure to ultraviolet light. The effect of visible light is not clearly established, although it appears to play some small part. Certain differences which arise when specimens are exposed under different filters may be due to light intensity which can affect the time a surface is wet with moisture.

Technical Papers on Corrosion Welcomed

Authors of technical papers on corrosion are invited to submit them for review without invitation to the Editor of Corrosion. Write for "Guide for the Preparation and Presentation of Papers" sent free on request to prospective authors.

Corrosion of Carbon and Low-Alloy Steels
In Out-of-Pile Boiling-Water-Reactor Environment*

By D. C. VREELAND, G. G. GAUL and W. L. PEARL

Introduction

STAINLESS STEEL has been used as the basic construction material in most high-temperature water-cooled nuclear-power-reactor designs, primarily to minimize the problems of corrosion and of corrosion products passing into the recirculating water system. If carbon or low-alloy steel were substituted for stainless steel in high-temperature primary-coolant-system components, the potential economic and engineering gains would be:

1. Lower material cost.

2. Lower thermal expansion and better heat-transfer characteristics.

3. Greater availability in quantity and shelf items.

4. Greater number of manufacturers with carbon-steel fabrication experience in pressure vessels and piping.

5. Less serious radioactive problems from troublesome corrosion products such as cobalt-60.

6. Elimination of stress corrosion cracking problems in some reactor designs.

One of the main problems in the use of carbon or low-alloy steel is corrosion resistance.

Concurrent with participation by private industry in construction of nuclear-power plants, economics became more important, so any material resulting in a lower installed and operating cost than that obtained with stainless steel appears attractive. A recent study[1] revealed that $1,750,000 could be saved by substituting $2\frac{1}{4}$ percent chromium-1 percent molybdenum alloy steel for stainless steel in a 300 MW dual-cycle boiling-water plant, exclusive of the reactor vessel.

The Atomic Energy Commission (AEC) has investigated the possibility of using carbon or low-alloy steel in pressurized-water reactor systems and the results have been promising enough that a pressurized-water reactor in which carbon steel is used for primary system components has been built at the National Reactor Test Station in Idaho.[2]

For carbon steel to be used successfully in pressurized-water-reactor primary systems, it is believed necessary (1) to keep the oxygen content of the water at very low levels, and (2) to raise the pH of the water to the range 10.5 to 11.5. Experience in steam-power plants and results of substantial AEC-sponsored testing support these conclusions. In water-cooled nuclear reactors, however, water can be

decomposed radiolytically to oxygen and hydrogen.

The problem of oxygen in the reactor-coolant water resulting from such radiolytic water-decomposition was resolved early for pressurized-water reactors by introducing an excess of hydrogen into the coolant water.[3] The radiolytic recombination of hydrogen and oxygen to form water was accelerated so that little or no residual free oxygen remained in the water.

Boiling-water reactors differ from pressurized-water reactors in that the steam generated in the reactor passes directly to the turbine. An example is shown in Figure 1, which is a simplified flow diagram of the Dresden Boiling Water Reactor. Maintaining an excess of externally added hydrogen to force recombination of radiolytic oxygen and hydrogen in a boiling-reactor system where the noncondensible gases exit through the stack would be impractical. Oxygen from radiolytic decomposition of the water, therefore, is expected to be present in the steam and the recirculating water of a boiling-water reactor. Determined by the specific characteristics of the particular boiling-water reactor under consideration, the oxygen content of the steam will be 10 to 30 ppm,[4] with a dynamic-equilibrium quantity in the recirculating water. As a result of water decomposition, total oxygen present will be in the stoichio-

Abstract

Results are reported of extensive corrosion testing of carbon and low-alloy steels in a dynamic test loop simulating the various environments found in a nuclear boiling-water-reactor system. Quantitative data and metallographic and visual observations of specimens tested in saturated steam, saturated water and a steam-water mixture, all at 545 F and 1000 psi are presented. Water and steam conditions are based on 10 to 20 ppm oxygen in the steam with a 1:8 stoichiometric ratio of hydrogen to oxygen, a condition representative of the hydrogen and oxygen formed in a boiling-water reactor from radiolytic water decomposition. The water is maintained at pH 7, high purity with no other additives. A description of the boiling-water dynamic-test facilities and operating procedures is included.

Total corrosion and corrosion product released into the system is measured. No appreciable difference was noted among corrosion rates of carbon steels, high-strength low-alloy steels and alloy steels studied, although all showed higher rates than the AISI Type 300 series stainless steels tested. Comparisons also were made with other stainless steels. No selective attack was noted on welded specimens.

Corrosion rates obtained on the carbon and low-alloy steels are lower than those obtained by other investigators on similar materials in test loops simulating pressurized water-reactor systems operated at high pH (> 10) with only hydrogen gas in the water. The iron-to-system rates in the present tests were appreciably lower than those in similar tests in high pH and neutral pH systems with a hydrogen environment.   8.4.5, 6.2.3, 6.2.4

metric ratio of eight to one with the total hydrogen.

References in the literature indicate that some concentrations of dissolved oxygen in water not only do not accelerate corrosion of carbon or low-alloy steel but

Figure 1—Dual-cycle boiling water reactor.

Figure 2—Schematic diagram of boiling water test loop.

Vreeland

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Figure 3—Test holder and specimens.

actually inhibit corrosion. This inhibition apparently can occur at either room or higher temperatures. There is no agreement as to the amount of dissolved oxygen necessary in water to cause inhibition: Uhlig[5] reports that at 86 F and at a velocity of 0.25 fps the corrosion rate of mild steel in distilled water is 60 mpy at about 22 ppm dissolved oxygen, and 5 mpy at about 34 ppm dissolved oxygen. Frese[6] found that at 72 to 77 F, mild steel showed maximum corrosion rate in distilled water at a point below 40 ppm dissolved oxygen; at higher oxygen content the corrosion rate decreased. At low oxygen content, corrosion products were loose and fluffy; at higher oxygen content they were hard and adherent, and

indicated a more protective film. Vernon[7] suggested increased aeration, rather than deaeration, to reduce corrosion of steel in natural water or dilute-salt solutions. Cox and Roetheli[8] found that at room temperature the corrosion rate of mild steel in water with dissolved oxygen appeared to be proportional to the oxygen content up to about 10 ppm oxygen; above 10 ppm oxygen the rate appeared to level off. Copson[9] points out that there is an interrelation between water velocity and oxygen concentration on the corrosion of carbon steel.

In higher-temperature water, Breden

TABLE 1—Composition of Steels, Percent

Steel	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Others
Structural Carbon Steels										
AISI C 1008	0.06	0.43	0.005	0.028	0.01	ND*	ND	ND	ND	....
**AISI C 1020	0.21	0.54	0.011	0.029	0.05	ND	ND	ND	ND	....
ASTM A 212 Grade B	0.27	0.92	0.016	0.028	0.22	ND	ND	ND	ND	....
ASTM A 285 Grade C	0.17	0.54	0.011	0.032	0.08	ND	ND	ND	ND	....
ASTM A 201 Grade A	0.20	0.55	0.015	0.029	0.24	ND	ND	ND	ND	....
High-Strength Low-Alloy Steels										
USS TRI-TEN	0.15	0.95	0.014	0.039	0.20	0.29	ND	ND	ND	V = 0.09
USS COR-TEN	0.08	0.45	0.100	0.026	0.47	0.29	0.28	0.76	ND	....
Alloy Steels										
ASTM A 302 Grade B	0.20	1.29	0.014	0.011	0.18	ND	ND	ND	0.55	....
AISI 4130	0.30	0.51	0.010	0.019	0.26	ND	ND	1.05	0.20	....
AISI 4340	0.41	0.86	0.012	0.018	0.29	ND	1.75	0.77	0.25	....
USS "T-1"	0.15	0.83	0.013	0.025	0.19	0.25	0.85	0.60	0.48	V = 0.05, B = 0.004
**USS "T-1"	0.13	0.81	0.025	0.023	0.18	0.32	0.82	0.57	0.50	V = 0.05, B = 0.002
Stainless Steels										
AISI Type 502	0.07	0.53	0.019	0.012	0.44	ND	ND	5.00	0.54	....
AISI Type 410	0.10	0.35	0.016	0.017	0.28	ND	ND	12.09	ND	....
AISI Type 430	0.05	0.46	0.020	0.007	0.32	ND	ND	16.26	ND	....
USS TENELON	0.08	14.52	0.017	0.004	0.70	ND	ND	18.23	ND	N = 0.55
AISI Type 202	0.10	7.48	0.032	0.006	0.47	ND	4.72	17.85	ND	N = 0.13
AISI Type 302	0.10	1.58	0.022	0.017	0.45	ND	9.50	18.82	ND	....
AISI Type 304	0.06	1.60	0.040	0.016	0.58	ND	9.40	18.80	ND	....
**AISI Type 304 L	0.03	1.28	0.019	0.015	0.35	ND	9.52	18.54	ND	....
USS Stainless "W"	0.07	0.63	0.009	0.021	0.76	ND	6.42	17.08	ND	Al = 0.28, Ti = 0.92

* Not determined.
** Material used for dual-metal specimens.

TABLE 2—Thermal Treatment and Hardness Values of Steels Tested

Steel	Thermal Treatment	Rockwell Hardness Value
Structural Carbon Steel		
AISI C 1008	Hot rolled	B 60
ASTM A 212 Grade B	Normalized	B 78
ASTM A 285 Grade C	Hot rolled	B 92
ASTM A 201 Grade A	Normalized	B 62
High-Strength Low-Alloy Steels		
USS TRI-TEN	Hot rolled	B 85
USS COR-TEN	Hot rolled	B 84
Alloy Steels		
ASTM A 302 Grade B	Normalized	B 66
AISI 4130	1650 F, oil quenched, tempered for 2 hours at 1100 F, air-cooled	C 29
AISI 4340	1750 F, air-cooled, tempered for 2 hours at 1250 F	C 22
USS "T-1"	1700 F, water quenched, tempered for ½ hour at 1175 F	C 26
Stainless Steel		
AISI Type 502	Annealed	B 81
AISI Type 410	Annealed	B 76
AISI Type 430	Annealed	B 85
USS TENELON	Annealed	B 100
AISI Type 202	Annealed	B 90
AISI Type 302	Annealed	B 78
AISI Type 304	Annealed	B 78
USS Stainless "W"	1950 F, aged for 30 minutes at 1000 F	C 43

and co-workers[10] indicate "good" results for A 212 B steel in water containing a large concentration of oxygen and "poor" results in water containing much less oxygen. Moore[11] tested carbon steel at 482 F, 26 fps water velocity, and at 6, 30, 90 and 400 psi oxygen. Tests with lower pressures of oxygen produced heavy scales of corrosion products that were easily removed and were identified as being predominantly Fe_3O_4. Corrosion rates in lower oxygen-pressure tests varied from 5 to 16 mpy. In tests at higher oxygen pressures, the oxide films produced on specimens were thin and very adherent, and showed more Fe_2O_3 than those in the lower oxygen-pressure systems. Corrosion rates in the higher oxygen-pressure tests varied from 3 to 6 mpy. Seebold[12] concludes from his tests that the presence of a proper concentration of oxygen in water inhibits the corrosion of carbon steel in loop systems at temperatures up to 600 F.

There is disagreement on the effect of pH above neutral on the corrosion of carbon steel. The *Corrosion and Wear Handbook*[13] indicates that the corrosion rate of carbon steel at temperatures of 500 to 600 F can be reduced fourfold by the use of water of pH 10.5 to 11.5, as compared to the use of neutral pH water. However, Bloom[14] et al. report no effect on the corrosion of carbon steel at 600 F when the pH of the test water was raised from neutral to 10.6. Douglas and Zyzes[15] also found no effect on the corrosion of carbon steel from 464 to 680 F when the pH of the test water was raised from neutral to about 12.

The present work was conducted to determine the corrosion behavior of carbon and low-alloy steels in the environment unique to boiling-water reactor systems. Several types of stainless steels were also tested.

Experimental Procedure

Materials

Materials tested in this investigation included steels generally classified as structural carbon steels, high-strength low-alloy steels, alloy steels and stainless steels. The chemical compositions of the steels are listed in Table 1 and their thermal treatment and hardness values are listed in Table 2. All the steels were obtained from regular mill products and are representative of commercially available materials. The 3 by ¾-inch test specimens varied from 1/16 to ⅛-inch in thickness. The specimens were fabricated by machining them to the proper dimensions and then surface-grinding them to a 120-grit finish. A number of welded specimens were also tested. For the dual-metal welded specimens AISI C 1020 carbon steel or USS "T-1" high-yield strength, heat-treated constructional alloy steel welded to AISI Type 304 L stainless

steel was used. The shielded metal-arc process was used to join the materials. For welded specimens composed of only one steel, a bead was deposited on the specimens by means of the shielded metal-arc process. Table 3 shows the American Welding Society-American Society for Testing Materials (AWS-ASTM) classification of the electrodes used for welding the various materials and the ASTM requirements for the composition of the deposited weld metal from the electrodes.

The specimens were identified, washed, degreased in acetone, dried and weighed. After the test, the specimens were weighed, examined by means of a low-power microscope and descaled electrolytically with the specimen as cathode and with a lead anode in a solution consisting of 5 percent sulfuric acid inhibited with ½-gram ethyl quinolinium iodide per liter. The specimens were then weighed to obtain descaled corrosion

TABLE 3—Electrodes Used for Fabricating Welded Specimens and ASTM Chemical Requirements for Deposited Weld Metal
(Single values shown are maximum percentages)

Weld-Specimen Base Material	AWS-ASTM Electrode Classification Number	ASTM Chemical Requirements for Deposited Weld Metal							
		C	Mn	P	S	Si	Ni	Cr	Mo
USS "T-1" to AISI Type 304L	E 308	0.08	2.50	0.04	0.03	0.90	9.0-11.0	18.0-21.0	....
AISI C1020 to AISI Type 304L	E 308	Same	....	....	....	....	....	....	....
AISI Type 304	E 308	Same	....	....	....	....	....	....	....
USS TENELON	E 308	Same	....	....	....	....	....	....	....
ASTM A 212 Grade B	E 7016-A1	0.12	0.90	....	0.04	0.60			0.40-0.65
ASTM A 285 Grade C	E 7016-A1	Same		....	0.04	0.60			
ASTM A 302 Grade B	E 7016-A1	Same		....	0.04	0.60			
AISI 4130	E 10016-D2	0.15	1.65-2.00	....	0.04	0.60			0.25-0.45
AISI 4340	E 10016-D2	Same		....	0.04	0.60			0.25-0.45
USS "T-1"	E 10016-D2	Same							
AISI Type 410	E 410	0.12	1.00	0.04	0.03	0.90	0.60	11.0-14.0	....
AISI Type 430	E 430	0.10	1.00	0.04	0.03	0.90	0.60	15.0-18.0	....

TABLE 4—Loop Conditions During Test

Length of Test, hr.		74	210	309	697	771	936	1008	1009	1029	1945	2010
Temperature, F...	Steam	546	546	546	546	546	†	546	546	546	546	546
	Steam-water	546	546	546	546	546	546	546	546	546	546	546
	Saturated-water	546	†	546	546	546	546	546	546	546	546	†
	Subcooled-water	530	530	537	535	535	†	537	537	530	537	530
Oxygen Content, ppm...........	Steam (range) (mean)	7.0-25.0 16.0	4.0-30.0 ††	6.5-21.0 13.0	6.3-33.0 15.6	6.3-33.0 15.6	† †	9.0-22.0 13.7	5.0-34.0 14.4	50-200 ††	5.0-34.0 14.6	4.0-200 ††
	Steam-water (range) (mean)	7.0-25.0 16.0	4.0-30.0 ††	6.5-21.0 13.0	6.3-33.0 15.6	6.3-33.0 15.6	13.2-23.0 14.7	9.0-22.0 13.7	5.0-34.0 14.4	50-200 ††	5.0-34.0 14.6	4.0-200 ††
	Saturated-water (range) (mean)	0.04-0.2 0.09	† †	0.04-0.4 0.1	0.04-0.18 0.08	0.04-0.2 0.08	0.07-0.2 0.1	0.05-0.3 0.1	0.02-0.2 0.08	† †	0.02-0.2 0.09	† †
	Subcooled-water (range) (mean)	0.2-1.0 0.6	0.4-2.0 ††	0.5-1.4 0.8	0.1-1.4 0.7	0.1-1.4 0.7	† †	0.5-3.0 1.0	0.3-1.3 0.6	1.0-5.0 ††	0.3-1.3 0.8	0.1-5.0 ††
Hydrogen, ppm in steam and steam-water (range) (mean)		1.0-3.0 2.0	0.5-3.8 ††	0.9-3.3 1.6	0.8-4.3 2.1	0.8-4.3 2.1	1.5-3.3 2.0	1.0-3.0 1.8	0.6-4.0 1.9	6-25 ††	0.6-4.0 2.0	0.5-25 ††
Time in hr after test start-up before oxygen and hydrogen contents were at desired level.		7	100	2.5	4	7*	3	4	4	3	4**	3***
pH (mean @ 68F).....................		6.8	6.8	6.1	6.1	6.1	6.2	5.9	6.0	6.8	6.1	6.6
Flow velocity, ft/sec steam-water, steam, saturated-water, subcooled-water........		11 6	11 6	11 6	11 6	11 6	11 6	11 6	11 6	11 6	11 6	11 6
Chloride, ppm....................		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pressure, psig.....................		1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Water resistivity, megohm-cm (mean).......		4.0	6.0	8.0	5.8	5.8	8.0	10.0	7.1	>1	7.6	>1

* Test shut down after 74 hr operation; additional start-up involved 4 more hr after test start-up before oxygen and hydrogen were at desired level.
** Test shut down after 1009 hr operation; additional start-up involved 3 more hr after test start-up before oxygen and hydrogen were at desired level.
*** Test shut down after 1029, 1239, 1313 hr of operation; additional start-ups involved 111 more hr after test start-up before oxygen and hydrogen were at desired level.
† No specimens tested in this environment.
†† Range of values is more significant indication of conditions than a calculated mean.
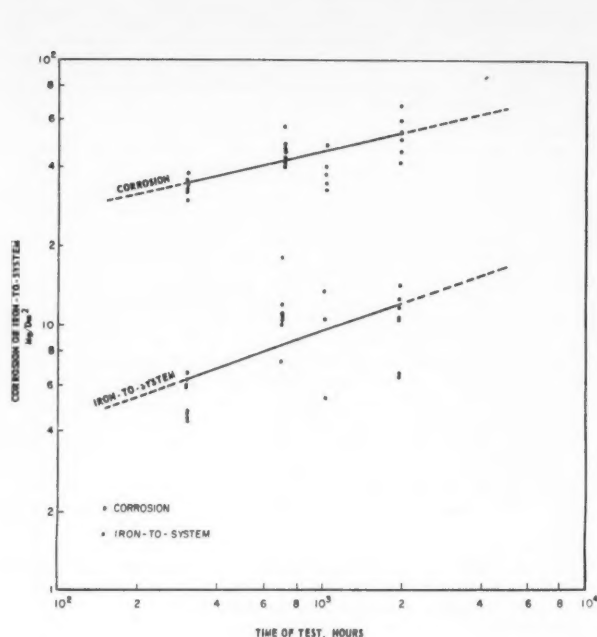
Figure 4—Corrosion and iron-to-system in saturated water of steels containing up to 5 percent chromium.
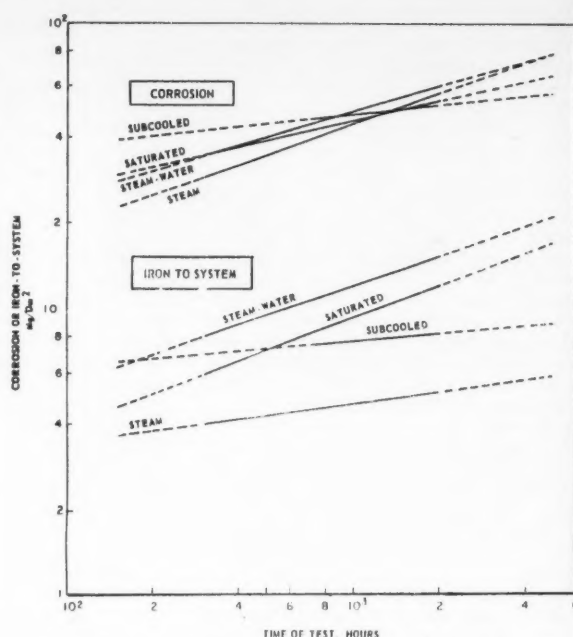
Figure 5—Effect of environments on corrosion and iron-to-system of steels containing up to 5 percent chromium.

losses. Selected specimens were examined metallographically.

Method

The specimens were tested in a boiling-water loop, shown in schematic diagram in Figure 2. Internal heaters generate steam in the heater section; the steam-water mixture flows through a test holder to the primary steam drum where it is separated into saturated-steam and saturated-water phases. The steam then flows through a test holder, is condensed in the primary condenser, and the resulting water flows through a heat exchanger into the sub-cooled section of the loop and is returned to the heater section. The saturated water from the primary steam drum flows through a test holder and is combined with the steam condensate going to the heat exchanger.

Figure 3 is a photograph showing specimens being inserted into a typical holder. Specimens are bolted to the holder cover-plates with stainless-steel bolts and separated by stainless-steel spacers. Crevices and galvanic contact thus are present between the stainless-steel spacers and the specimens. During the test, the holder is placed inside the loop piping. The main lines of the loop are constructed of AISI Type 304 stainless-steel Schedule-80 pipe 1½ inches in diameter. During the tests, temperatures were 546 F in the steam, steam-water and saturated-water sections and about 537 F in the sub-cooled water section. The pressure was 1000 psig. Water and steam conditions were based on 10 to 20 ppm oxygen in the steam with a 1:8 stoichiometric ratio of hydrogen to oxygen, a condition representative of the hydrogen and oxygen formed in a boiling-water reactor from radiolytic water decomposition. Gaseous oxygen and hydrogen were added to the

loop by means of gas addition bombs, which were inserted into a bypass system in the loop. Oxygen analyses of the loop water were made by gas-chromatography and Winkler methods, hydrogen analyses of the loop water by the gas-chromatography method. The velocity of steam, saturated water and sub-cooled water past the test specimens was about 6 fps; the velocity of steam-water past the test specimens was about 11 fps. Loop water was maintained at neutral pH with no chemical additives. The water resistivity varied from about 4 to 10 megohm-centimeters during the various test runs conducted. The duration of the test runs ranged from 74 to 2010 hours. Loop conditions during the various test runs are summarized in Table 4.

At the start of the tests, after the specimen holders were placed in position, high-purity non-degassed water was introduced into the loop. As the water was heated, the loop was continuously blown down until gas analyses indicated that oxygen in the steam was less than ½ ppm. Oxygen and hydrogen additions then were made to bring the loop to the desired operating conditions. Usually about four hours elapsed from start-up until the oxygen and hydrogen contents of the loop water were at the desired level.

Discussion of Results

Corrosion results obtained are summarized in Table 5 and the iron-to-system results in Table 6. The values reported are in most cases the mean of the results from two or more specimens. All corrosion results are reported on a descaled basis in milligrams per square decimeter (mg/dm²). For purposes of comparison, 2000 mg/dm² is equivalent to 0.001-inch of metal loss.

Special emphasis has been given to the

iron-to-system data in this work because of the deleterious effects of radioactive corrosion products formed, accumulated, transported and deposited throughout a nuclear-reactor cooling system. The iron-to-system values were calculated from the following equation: iron-to-system = descaled weight loss — iron calculated to be in the adherent oxide (assuming the oxide is Fe_3O_4).

Effects of Metal Composition

A logarithmic plot of the amount of corrosion and iron-to-system against time in the saturated-water environment is shown in Figure 4 for all the steels tested that contained up to 5 percent chromium. The lines are fitted to the points by the method of least squares. Two points for iron-to-system values of <1 were omitted from Figure 4, since it was believed that these values might possibly be in error and omitting them would result in a more conservative presentation of the results. The scatter of data was within normal test variation and showed no clear difference between any steels tested containing up to 5 percent chromium. Similar results were found in the steam, steam-water, and subcooled water environments.

It can be noted by referring to Table 5 that some steels containing up to 5 percent chromium may not appear to follow the general corrosion trend. In particular, the corrosion of USS Tri-ten and USS Cor-ten in steam-water, saturated water, and saturated steam appears to be leveling off as time of test increases from 309 hours to 1008 hours when compared with results for some of the other steels. However, it can also be seen in Table 5 that ASTM A 201 Grade A steel (a structural carbon steel) exposed in the same tests corroded about the same amount as did USS Tri-ten and USS Cor-ten. There-

fore, it is believed that unknown factors inherent in the 1008-hour run kept corrosion low and that USS Tri-ten and USS Cor-ten have the same corrosion behavior in simulated boiling-water-reactor-environment as the other steels containing up to 5 percent chromium.

Effect of Exposure in Steam, Steam-Water or Water

Figure 5 is a comparison of differences in corrosion and iron-to-system for specimens exposed to saturated steam, saturated water, a mixture of saturated steam and water and sub-cooled water. Lines were plotted by using the method of least squares for corrosion and iron-to-system for all steels tested containing up to 5 percent chromium. No major effect on corrosion or iron-to-system was noted because of exposure in the steam, steam-water, saturated water or sub-cooled water environments. Of particular interest is the fact that exposure of the steels to the boiling water did not produce any special corrosive effects.

Gas Content and pH of Water

Instantaneous corrosion rates obtained in saturated water are shown in Figure 6 and compared to the extensive work sponsored by the Naval Reactors Branch of the AEC for pressurized-water-reactor applications of carbon steel. The AEC results are well documented, and include a progress report of tests in the pH range of 10 to 12 by Blaser and Owens[16] and a summary of the results of tests at pH 7 to 11.5 by Tackett, Brown and Esper.[17] AEC tests generally were run with hydrogen and little or no oxygen in the water, as is presently the practice in pressurized water reactor applications. Plot of the instantaneous rates in Figure 6 was calculated by obtaining the first derivative of the equation for the least-squares line for corrosion in saturated water (from Figure 4) and is plotted with similarly calculated lines from Blaser and Owens[16] and Tackett, Brown and Esper's[17] work on carbon steel. The corrosion rates in the boiling system containing oxygen and hydrogen are much lower than the corrosion rates in a pressurized system containing only hydrogen, both at a pH of about 7. This difference apparently increases with time after about 300 hours exposure, as is shown by the flattening out of the curve for the pressurized system results at pH 7. Increasing the pH to the range of 10 to 12 of the pressurized-system water containing hydrogen decreased the corrosion rate, but the rates in the boiling system containing oxygen and hydrogen were still somewhat lower.

A similar comparison of iron-to-system rates was made in Figure 7. The differences were even greater than those noted

TABLE 5—Corrosion in Mg/Dm²

Time, Hours	309	697	771	1008	1009	1029	1945	2010	309	697	771	1008	1009	1029	1945	2010
Steel	Steam-Water								Saturated Steam							
AISI C 1008	..	..	..	..	..	62	..	82	..	47	..	..	..	..	..	93
ASTM A 212 Grade B	36	56	..	..	55	..	62	..	27	36	..	..	47	..	45	..
ASTM A 285 Grade C	..	56	..	..	..	..	..	..	..	..	34	..	..	..	..	..
ASTM A 201 Grade A	40	..	..	42	..	..	..	..	35	..	..	37	..	..	..	..
USS TRI-TEN	36	..	..	38	..	..	..	..	25	..	..	33	..	..	..	..
USS COR-TEN	34	..	..	34	..	..	..	..	30	..	..	35	..	..	..	..
ASTM A 302 Grade B	40	48	..	..	..	..	65	..	36	38	..	..	..	..	67	..
AISI 4130	31	49	..	..	..	..	59	..	34	32	..	..	..	..	51	..
AISI 4340	34	46	..	..	..	..	54	..	33	39	..	..	..	..	57	..
USS "T-1"	34	..	..	..	..	56	..	69	30	35	..	..	..	..	..	59
AISI Type 502	31	..	..	..	42	..	48	..	23	..	..	..	36	..	40	..
AISI Type 410	..	..	37	..	..	..	..	..	..	..	..	..	..	15	..	30
AISI Type 430	..	..	22	..	..	..	..	..	..	..	..	..	..	20	..	26
USS TENELON	5	..	16	..	..	..	..	..	10	..	23	..	..	..	..	..
AISI Type 202	2	..	..	..	11	..	..	..	9	..	..	..	10	..	..	..
AISI Type 302	..	..	15	..	..	..	..	..	..	..	17	..	..	..	..	..
AISI Type 304	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
USS Stainless "W"	3	..	..	..	8	..	..	..	8	..	..	..	15	..	..	..
	Saturated Water								Sub-cooled Water							
AISI C 1008	..	56	..	..	..	..	67	..	..	..	..	..	..	57	78	..
ASTM A 212 Grade B	32	46	..	..	48	..	53	..	..	58	..	..	44	..	53	..
ASTM A 285 Grade C	..	48	..	..	..	..	..	..	..	65	..	..	..	..	..	..
ASTM A 201 Grade A	38	..	..	37	..	..	..	..	..	..	..	40	..	..	..	..
USS TRI-TEN	33	..	..	32	..	..	..	..	..	..	..	31	..	..	..	..
USS COR-TEN	34	..	..	35	..	..	..	..	..	..	..	30	..	..	..	..
ASTM A 302 Grade B	35	46	..	..	..	..	59	..	..	62	..	..	..	..	63	..
AISI 4130	35	42	..	..	..	..	54	..	..	48	..	..	..	..	44	..
AISI 4340	36	42	..	..	..	..	50	..	..	46	..	..	..	..	58	..
USS "T-1"	32	41	..	..	..	..	42	..	..	..	..	..	..	40	..	57
AISI Type 502	30	..	..	..	40	..	46	..	..	..	..	..	31	..	37	..
AISI Type 410	..	..	28	..	..	..	33	..	..	..	..	38	..	..	..	..
AISI Type 430	..	..	19	..	..	..	..	..	..	..	..	29	..	..	..	..
USS TENELON	2	..	16	..	..	..	23	..	..	..	..	26	..	..	..	..
AISI Type 202	1	..	..	..	9	..	12	..	..	..	..	..	9	..	..	..
AISI Type 302	..	12	..	..	..	..	..	..	..	..	..	..	..	26	..	..
AISI Type 304	3	..	..	..	12	..	14	..	..	..	..	..	5	..	..	..
USS Stainless "W"	8	..	..	..	4	..	3	..	..	..	..	..	5	..	..	..
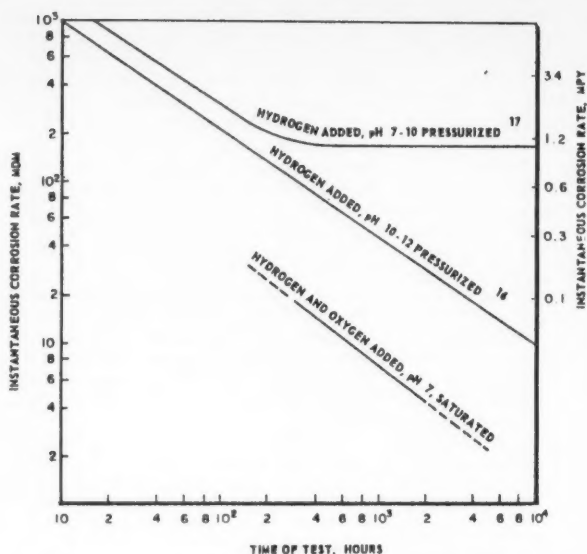
Figure 6—Comparison of instantaneous corrosion rates of steels containing up to 5 percent chromium.
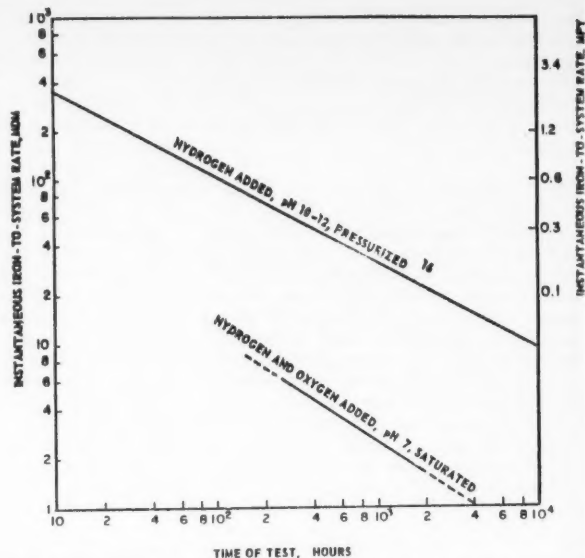
Figure 7—Comparison of iron-to-system rate of steels containing up to 5 percent chromium.

for corrosion rates; the iron-to-system rates in the boiling system containing oxygen and hydrogen were again lower. Results for a pressurized system at pH 7 were not plotted in Figure 7, because sufficient data were not available to establish the location of a generalized curve. However, the iron-to-system rates in a pressurized system are higher at pH 7 than at pH 10 to 12.[17]

In an attempt to define the role of oxygen, comparison tests were made between exposures in a simulated pressurized water reactor system and a boiling water reactor system, both operated at pH 7. The coupons were exposed to water containing 6 ppm hydrogen and less than 0.1 ppm oxygen in the pressurized test and to saturated water containing about 0.1 ppm (0.02 to 0.4 ppm) oxygen and the stoichiometric amount of hydrogen (~0.01 ppm) in the boiling test. Results listed in Table 7 confirm the differences in corrosion and iron-to-system for the two systems.

Examination of the specimens revealed that the oxide formed on the specimens exposed in the boiling water loop (with comparable volumes of oxygen and hydrogen present) was much more adherent and presumably protective than the oxide layer formed in the pressurized water loop with a large excess of hydrogen and little oxygen. Thus, the quantity of hydrogen as well as oxygen appears important in the formation of an adherent protective oxide layer on carbon and low-alloy steels.

A comparison from Tables 5 and 6 of the amount of corrosion and iron-to-system for the 1029-hour run containing 50 to 200 ppm oxygen in the steam with the results from 1008- and 1009-hour runs containing about 14 ppm oxygen in the steam indicates that in the presence of oxygen no significant effect of the total gas present exists within the range tested. In all cases the stoichiometric quantity of hydrogen was present. In making this

comparison, the steels containing up to 5 percent chromium should be compared.

Local Attack

After the tests, all corrosion specimens were examined for evidence of local attack including crevice corrosion and galvanic corrosion in the areas under the stainless-steel spacers used in mounting the specimens in the loop. Visually, no local attack was noted. However, the use of a low-power microscope (25-40X) showed that the tested steels containing up to 5 percent chromium were generally, but not always, subject to very slight localized attack or pitting and also to very slight crevice corrosion. Typical dimensions of an area of localized attack are 1 mil in depth and 3 mils in width. No sign of localized attack was found on the steels tested in the 1029-hour test in which the oxygen as measured in the steam was kept above 50 ppm with the stoichiometric amount of hydrogen. The local attack may occur during the part of the test when the loop is being brought up to temperature before test conditions are reached. This hypothesis is strengthened by the fact that the areas of local attack do not appear to increase in size, depth or number as the test time increases.

Effect of Start-Up Conditions

Beneficial effects of the oxygen and hydrogen were well demonstrated in a 210-hour test in which no gas was added for the first 100 hours. The amount of corrosion and iron-to-system are compared in Table 8 with a 309-hour run in which hydrogen and oxygen were added within the first 3 hours. A significantly lower total amount of corrosion and iron-to-system occurred in the longer run, protected early by the oxygen and hydrogen. A 74-hour run in which no gas was added for 7 hours is also shown in Table 8. Although this test ran only one-fourth the time, the total corrosion was greater than in the 309-hour run.

The protective nature of the film found in oxygen and hydrogen was shown in a special test conducted concurrently with the above 210-hour test. AISI C 1008 steel was first exposed in the 1029-hour test with oxygen and hydrogen added to the water within 3 hours of start-up. The amount of corrosion and iron-to-system was determined in the usual manner on some of the specimens exposed in the 1029-hour test. Other specimens from which the corrosion products had not been removed were then exposed in the above 210-hour test with no added oxygen or hydrogen in the water for the first 100 hours. In addition, unexposed specimens were included in the 210-hour test. Results are tabulated in Table 9. Not only did the oxide on the pre-exposed coupons reduce the corrosion rate in the more corrosive environment but total corrosion of exposed coupons for the full 1239 hours was less than that of the coupons exposed for only 210 hours of which the first 100 was in the absence of oxygen and hydrogen.

Tests of Welded Specimens

Tests were conducted with the welded specimens shown in Table 3. Stainless steel welded specimens were exposed for 936 hours in only the saturated-water environment. Welded specimens of the other steels were exposed in saturated water and also in steam-water environments for 936 hours. Because of the possibility that stainless steel might be welded to carbon or low-alloy steel in a reactor system that included carbon or low-alloy steel as a construction material, tests were conducted with dual-metal specimens consisting of AISI Type 304L stainless steel welded to AISI C 1020 steel or to USS "T-1" steel. The areas of stainless and carbon or "T-1" steel were about equal in these specimens. The dual-metal weld specimens were tested for 1008 hours in steam, steam-water, saturated water and sub-cooled water environments in the boiling-water

TABLE 6—Iron-to-System in Mg/Dm²

Time, Hours	309	697	771	1008	1009	1029	1945	2010	309	697	771	1008	1009	1029	1945	2010
Steel	Steam-Water								Saturated Steam							
AISI C 1008	..	..	..	..	..	14	..	23	..	7	..	..	..	..	..	13
ASTM A 212 Grade B	9	21	..	..	17	..	19	..	2	6	..	..	4	..	6	..
ASTM A 285 Grade C	..	16	..	..	..	..	..	..	..	7	..	..	..	..	..	..
ASTM A 201 Grade A	9	..	..	4	..	..	..	..	4	..	..	2	..	..	..	..
USS TRI-TEN	11	..	..	3	..	..	..	..	2	..	..	4	..	..	..	..
USS COR-TEN	5	..	..	4	..	..	..	..	4	..	..	6	..	..	..	..
ASTM A 302 Grade B	10	14	..	..	..	..	16	..	3	6	..	..	..	..	3	..
AISI 4130	9	18	..	..	..	..	15	..	3	4	..	..	..	..	6	..
AISI 4340	4	10	..	..	..	..	10	..	4	12	..	..	..	..	4	..
USS "T-1"	7	..	..	..	..	12	..	20	<1	4	..	..	..	..	..	9
AISI Type 502	9	..	..	..	14	..	13	..	<1	..	..	..	..	3	2	..
AISI Type 410	..	..	18	..	..	..	..	..	..	..	..	..	..	..	2	2
AISI Type 430	..	..	12	..	..	..	..	..	..	..	..	..	..	..	2	2
USS TENELON	<1	3	..	..	..	..	..	..	<1	..	3	..	..	..	..	..
AISI Type 202	<1	..	..	3	..	..	..	..	<1	..	..	..	..	<1	..	..
AISI Type 302	..	..	1	..	..	..	..	..	..	..	<1	..	..	..	..	..
AISI Type 304	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
USS Stainless "W"	<1	..	..	..	<1	..	..	..	<1	..	..	..	..	4	..	..
	Saturated Water								Sub-cooled Water							
AISI C 1008	..	11	..	..	..	..	11	..	..	..	..	..	..	..	8	7
ASTM A 212 Grade B	5	12	..	..	14	..	14	..	..	10	..	..	11	..	10	..
ASTM A 285 Grade C	..	11	..	..	..	..	..	..	..	9	..	..	..	..	..	..
ASTM A 201 Grade A	6	..	..	5	..	..	..	..	..	..	..	<1	..	..	..	..
USS TRI-TEN	..	..	..	<1	..	..	..	..	..	..	..	<1	..	..	..	..
USS COR-TEN	7	..	..	<1	..	..	..	..	..	..	..	<1	..	..	..	..
ASTM A 302 Grade B	6	11	..	..	..	..	13	..	..	10	..	..	..	..	8	..
AISI 4130	4	18	..	..	..	..	12	..	..	8	..	..	..	..	7	..
AISI 4340	5	8	..	..	..	..	7	..	..	9	..	..	..	..	4	..
USS "T-1"	5	10	..	..	..	..	7	..	..	..	..	..	..	3	..	10
AISI Type 502	6	..	..	..	11	..	11	..	..	..	..	..	..	10	11	..
AISI Type 410	..	..	15	..	..	..	13	..	..	..	19	..	..	..	..	..
AISI Type 430	..	..	6	..	..	..	..	..	..	..	6	..	..	..	..	..
USS TENELON	<1	..	2	..	..	..	7	..	..	..	..	10	..	..	..	..
AISI Type 202	<1	..	..	2	..	..	3	..	..	..	..	..	..	2	..	..
AISI Type 302	..	<1	..	..	..	..	..	..	..	..	..	..	..	..	3	..
AISI Type 304	<1	..	..	2	..	..	2	..	..	..	..	..	..	..	..	..
USS Stainless "W"	<1	..	..	<1	..	..	<1	..	..	..	..	..	..	<1	..	..

test loop. Visual, low-power microscopic and metallographic examination revealed no traces of galvanic, selective, or accelerated corrosion in or near the weld zones of any of the welded specimens. The absence of accelerated attack on the carbon steel or alloy steel portions of the dual-metal welded specimens indicates that galvanic corrosion is not an important factor.

Stainless Steels

Several non-welded stainless steels listed in Tables 5 and 6 also were tested. The amount of corrosion (in mg/dm²) of the stainless steels containing over 12 percent chromium was less than the corrosion of the steels containing up to 5 percent chromium as shown in Table 5. Not enough work was done on the stainless steels containing over 12 percent chromium to permit listing them in order of corrosion resistance. Other investiga-

tors have found that austenitic and semi-austenitic precipitation-hardenable stainless steels have better corrosion resistance in 500 F, high-purity water than do ferritic or martensitic stainless steels.[18] Despite their low nickel content, the Cr-Mn-Ni (AISI Type 202) and the Cr-Mn-N stainless steels compared favorably in corrosion resistance with the other austenitic stainless steels tested. More data are required before a valid comparison between carbon and alloy steels and stainless steels can be made.

Summary

Out-of-pile corrosion tests of several commercially available steels were conducted in a dynamic-test loop that simulates the various environments found in a nuclear boiling-water-reactor system. The tests were at 546 F, 1000 psig; water and steam conditions were based on 10 to 20 ppm oxygen in the steam with a

TABLE 7—Comparison of Corrosion Tests of AISI C 1008 Steel in System with Low Oxygen and Varying Hydrogen Content

	Corrosion Mg/dm³	Iron-to-System Mg/dm³
Test in Non-Boiling Loop, 6 ppm Hydrogen, 0.1 ppm Oxygen, pH = 6.6, 500F, 1000 hr, Water Velocity = 17.9 fps, 1000 psig........	279	214
Test in Boiling Loop, about 0.01 ppm Hydrogen, about 0.1 (0.02-2) ppm Oxygen, pH = 6.1-6.8, 546F, 1945 hr, Water velocity = 6 fps, 1000 psig..............	67	11

1:8 stoichiometric ratio of hydrogen to oxygen; and the water pH was 7, with no other additives.

It is concluded from this work that under the test conditions:

1. There was little, if any, difference

TABLE 8—Corrosion of Specimens of ASTM A 302 B Steel Exposed to Steam-Water in Tests Showing Effect of Early Addition of Oxygen and Hydrogen to Test Water

Test Time, Hr.	Hours After Start-up Before Oxygen and Hydrogen Added	Corrosion Mg/dm^2	Iron-to-system Mg/dm^2
309*	2½	40*	10*
210	100	140	81
74	7	49	23

* From Tables 5 and 6.

TABLE 9—Corrosion of Specimens of AISI C 1008 Steel Exposed in Subcooled Water Showing Protective Effect of Oxide

Test time, hr.	Hours After Test Start-up Before Oxygen and Hydrogen Added	Corrosion Mg/dm^2	Iron-to-system Mg/dm^2
1029	3	57	8
210	100	147	80
1029 plus 210	3 in 1029-hr test plus 100 in 210-hr test	75	16

in corrosion among the various steels containing up to 5 percent chromium.

2. There was little, if any, difference in corrosion among the various steels tested that could be attributed to testing in the four available environments; that is, steam, steam-water, saturated water, or 10 degree sub-cooled water.

3. Corrosion results obtained on steels containing up to 5 percent chromium are lower than the results obtained by other investigators on similar materials in test loops simulating pressurized water-reactor systems operated at greater than pH 10 with hydrogen but no oxygen in the water. The corrosion release rate in the present tests was appreciably lower than that in similar tests in high pH and neutral pH systems with hydrogen but no oxygen in the water.

4. It is believed that the low corrosion observed on the steels containing up to 5 percent chromium is due to the presence of oxygen, or oxygen and hydrogen, which may help to form a more protective adherent oxide on the steel.

5. When carbon steel was exposed to water containing oxygen and hydrogen, the oxide formed appeared to protect the steel against corrosion when it was subsequently exposed to water that was low in oxygen and hydrogen content.

6. Some very slight indications of localized and crevice corrosion were found on the steels containing up to 5 percent chromium. It is not known whether this local attack occurs during test or during loop start-up before test conditions are reached.

7. Welded specimens of several stainless steels and steels containing up to 5 percent chromium, and also specimens of stainless steel welded to carbon steel or an alloy steel showed no signs of galvanic, selective, or accelerated attack in or near the weld zones.

8. Corrosion of stainless steels tested containing over 12 percent chromium was less than that of steels containing up to 5 percent chromium.

9. Galvanic corrosion between stainless steel and carbon steel or alloy steel did not appear to be an important factor.

Recommendations and Future Work

Promising results obtained in this program indicate that carbon and low-alloy steels are worth further consideration as materials of construction for boiling-water reactor systems. Several areas exist in which work should be and is being done to further prove the feasibility of carbon and low-alloy steels for use in boiling-water reactor systems. Some of these areas of necessary work are:

1. Stress-corrosion cracking: It is not believed that carbon and low-alloy steels are susceptible to stress-cracking under boiling-water-reactor conditions; however, confirmation testing is being conducted.

2. Role of oxygen and hydrogen: Tests are being conducted to further define the individual role of the oxygen and hydrogen content in accomplishing the corrosion inhibition observed in the above work.

3. Local attack of carbon and low-alloy steels: It should be determined if the very slight local attack observed occurred during loop start-up or during test. To prevent local attack in a boiling-water-reactor system constructed of carbon or low-alloy steel, it may be necessary to consider inhibiting or scavenging the oxygen from the water during periods when the reactor is not operating and when the water is at or near room temperature.

4. Oxide formation: Studies of the oxide formed on carbon and low-alloy steels under varying water conditions could be useful in further defining how carbon and low-alloy steels resist corrosion in high-temperature, high-purity water containing both oxygen and hydrogen.

5. Corrosion on heat-transfer surfaces: It should be determined whether corrosion of carbon and low-alloy steels in these systems will increase at heat-transfer surfaces.

6. Corrosion products: Knowledge concerning the effects of carbon and low-alloy steel corrosion products in these systems is needed.

7. Heat transfer. It should be determined how heat transfer will be affected by corrosion on carbon and low-alloy steel surfaces.

Acknowledgment

This report is the result of a cooperative program between United States Steel Corporation and General Electric Company. The authors thank the managements of these corporations for permission to publish these data.

Loop operations were under the direction of M. Siegler and were conducted by C. V. Collard and R. D. Houston.

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DISCUSSION

Question by W. Z. Friend, International Nickel Co., New York, N. Y.:

Were any stress-corrosion specimens of carbon or low-alloy steels included in the tests in high-temperature water containing hydrogen and oxygen? In view of the possibility of the presence of nascent hydrogen resulting from radiolytic decomposition of water as well as from the corrosion reaction, the question of hydrogen embrittlement of steel probably should be considered.

Reply by D. C. Vreeland.

A number of carbon and low-alloy steel stress-corrosion-cracking specimens of the U-bend type are being tested. This portion of the program is not completed, but to date, no cracking has been detected in the specimens that have been tested.

Any discussion of this article not published above will appear in December, 1961 issue.

Corrosion Characteristics of Iron-Aluminum And Iron-Chromium-Aluminum Alloys In High Temperature Petroleum Applications*

By R. B. SETTERLUND and G. R. PRESCOTT

Introduction

DURING THE past thirty years, interest in the iron-aluminum and iron-chromium-aluminum alloys has stemmed primarily from the excellent resistance to oxidation and desirable magnetic and electrical properties of these alloy systems.[1] Recent results of corrosion studies indicate that these alloys are resistant to corrosion by hydrogen sulfide and oil-ash corrosion. In view of the potential applications in the petroleum industry, the current alloy development program will be reviewed in terms of phase relationships, mechanical properties, and corrosion characteristics.

Iron-Aluminum-Alloys

Figure 1 shows that the binary system of iron and aluminum forms a solid solution up to 36 percent aluminum.[2] The alloy system undergoes both a magnetic-non-magnetic reaction, shown by the dashed line, and an order-disorder reaction in the region of 12 to 22 percent aluminum. In 1934, Sykes and Bampfylde[3] reported the results of an extensive investigation of the binary iron-aluminum alloys containing up to about 17 percent aluminum. The carbon content of the experimental alloys were in the range of .04 to .06 percent.

Abstract

This paper reviews the basic metallurgy of the iron-aluminum system and the status of alloy development programs. Published data are summarized dealing with the strength of iron-aluminum alloys at elevated temperature, oxidation resistance, and resistance to oil-ash corrosion. New data are presented on a series of iron-aluminum and iron-aluminum-chromium alloys exposed to various concentrations of hydrogen sulfide at several different temperatures.   6.2.2, 4.3.2, 4.4.2

Figure 2 is a plot of the relative oxidation resistance of the alloy series at various temperatures. The relative corrodibility was determined by dividing the loss in weight of each alloy by the loss in weight of the most resistant alloy. As shown by the curves, alloys containing about 8 percent aluminum are highly resistant to oxidation up to 1800 F. A 10 percent alloy shows useful resistance up to 2000 F.

The addition of aluminum to low-carbon iron increases the tensile strength and yield strength and tends to reduce elongation. The experimental alloys used by Sykes and Bampfylde show a sharp drop in elongation between 2 and 4 percent aluminum, (see Figure 3). The authors concluded that alloys containing up to 5 percent aluminum could be cold worked. Alloys containing between 5 and 16 percent could be hot worked. Over about 16 percent aluminum, the alloy would have to be used in the as-cast and ground state. Little or no commercial development followed this work because

Prescott   Setterlund

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R. B. SETTERLUND is a research engineer in the Metallurgy Section of the C. F. Braun & Co Research Department, Alhambra, Calif. He received his BS in engineering from the University of North Dakota in 1957. After graduation he worked for the Anaconda Company as an engineer in the Process Development Group of an uranium ore mill. Presently his work involves the fields of corrosion and welding research development. He is a member of NACE and is active in Technical Group Committee T-8B.
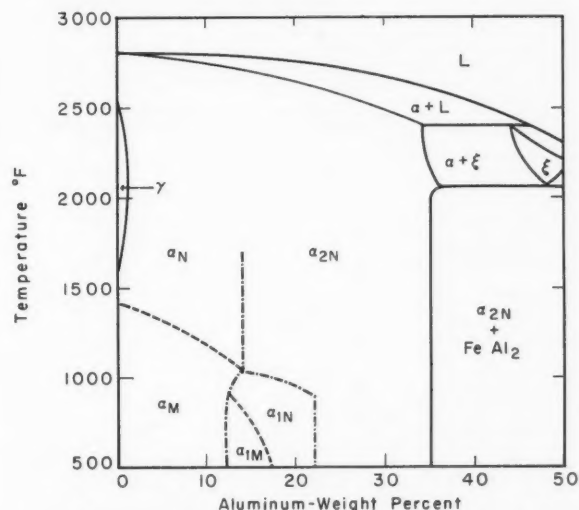
Figure 1—Iron-Aluminum phase diagram (taken from Fink and Willey[2]). Code to letters is as follows: α—ordered structure corresponding to Fe₃Al; α₂—ordered structure corresponding to Fe Al; N—nonmagnetic; M—magnetic.
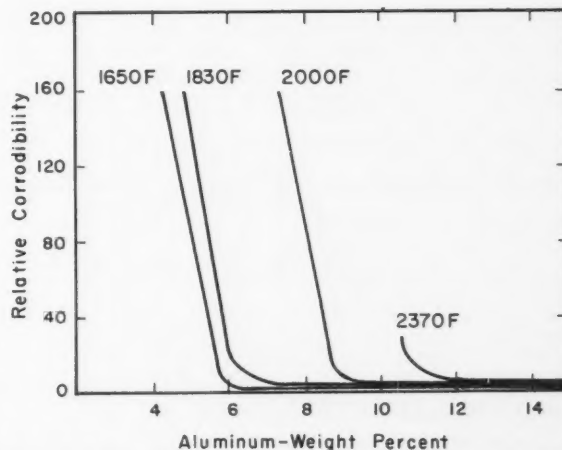
Figure 2—Relative oxidation resistance of iron-aluminum alloys (from Sykes and Bampfylde[3]).
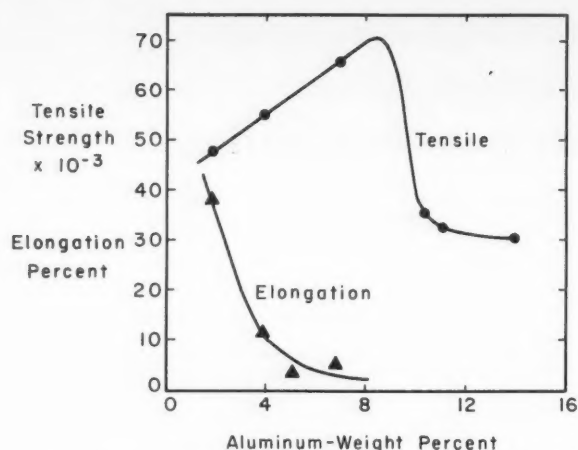
Figure 3—Mechanical properties of iron-aluminum alloys (Sykes and Bampfylde[3]).
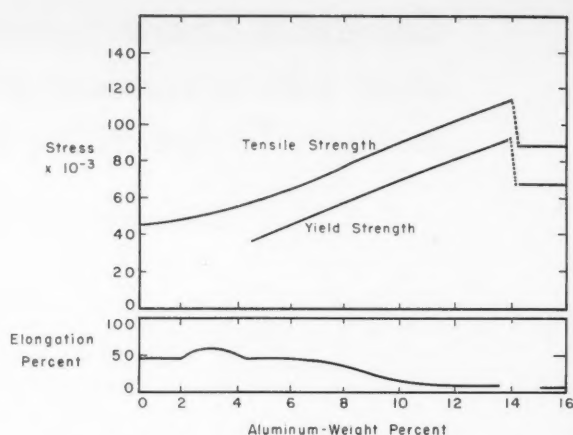
Figure 4—Room temperature properties of iron-aluminum alloys (from Morgan and Frey[7]).

of the difficulties in producing ductile wrought alloys with sufficient aluminum content for oxidation resistance.

In 1953, Nachman and Buehler[4,5] of the Naval Ordnance Laboratories developed two alloys for magnetic applications called Alfenol and Thermenol. Alfenol contains 16 percent aluminum and Thermenol contains 16 percent aluminum and 3 percent molybdenum. The addition of molybdenum resulted in a significant improvement in high temperature properties. By maintaining the rolling temperature at 1070 F, both of these alloys were rolled into thin strips one mil thick.

Thermenol has excellent oxidation resistance, good stress-to-rupture properties up to 1200 F, and comparatively low density. These advantages have stimulated further development work on iron-alumi-

num alloys. The early heats of Thermenol were low carbon single phase alloys that were subject to rapid grain growth. This resulted in an average elongation of about 3 percent at room temperature. Recent modifications of Thermenol with higher carbon contents and a small quantity of zirconium to inhibit grain growth show an average elongation of 9 percent.[6]

Recent work in other laboratories has resulted in considerable progress in producing ductile alloys through the use of improved melting techniques. This progress is summarized by comparing the room temperature elongation of iron-aluminum alloys obtained by Sykes and Bampfylde in 1934, see Figure 3, with more recent results obtained by the Ford Motor Company[7] as shown in Figure 4. Ford has obtained good ductility up to about 8 percent aluminum. The sharp
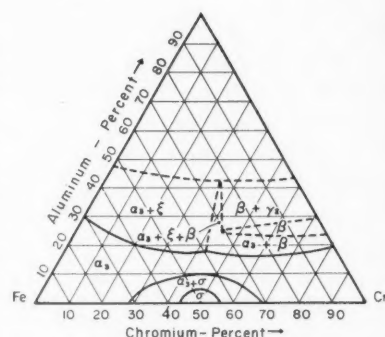
Figure 5—Phase diagram of Fe-Cr-Al at room temperature (from Kornilov[8]). Code to letters is as follows: α_3 iron-chromium-aluminum solid solution; σ sigma.
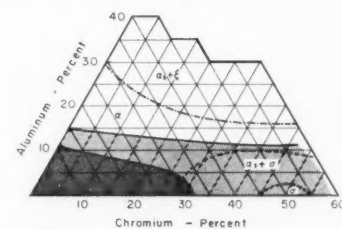
Figure 6—Effect of composition on hot and cold workability of Fe-Cr-Al alloys (from Kornilov[9]).

TABLE 1—Composition and Properties of Fe-Cr-Al Alloys Used in Russia[9]

	Alloy 1	Alloy 2	Alloy 3	Alloy 4
Composition:				
Carbon	.03—.07	.03—.07	.03—.07	.03—.07
Chromium	16—18	23—27	40—45	65—68
Aluminum	4.5—6.5	4.5—7.0	7.5—12.0	7.5—12.5
Properties:				
Structure	Single Phase	Single Phase	Single Phase	Single Phase
Tensile Strength	85,000—99,000	99,000—114,000	114,000—142,000	....
Elongation, percent	15—25	15—20	2—7	....
Formability	Hot and cold	Hot and cold	Hot only	....
Product	Wire, ribbon, and sheet	Wire, ribbon, and sheet	Wire, ribbon, and sheet	Cast elements
Uses	Rheostats, heating elements to 1830 F	Furnace elements to 2280 F	Furnace elements to 2460 F	Cast elements to 2730 F

TABLE 2—Composition and Typical Properties of Some Proprietary Electrical Resistors Used in the United States[10]

	AISI Type 406*	Alcress	Alchrome	Kanthal	Smith No. 10
Composition:					
Carbon	13.0	0.12	0.10	....	0.10
Chromium	13.0	12—15	19—21	20	35—37
Aluminum	4.0	2.0—4.0	5.25—6.5	5	7—9
Other	....	....	....	1.5—3.0 Co	....
Properties:					
Structure	Single Phase	Single Phase	Single Phase	Single Phase	Single Phase
Tensile Strength	87,000	85,000	100,000	118,000	....
Elongation, 2 inches	25	15	18	14	....
Limiting Service Temperature	1800 F	1740 F	2370 F	2280 F	2370 F

* Added to original list of proprietary alloys listed by Hessenbruch.
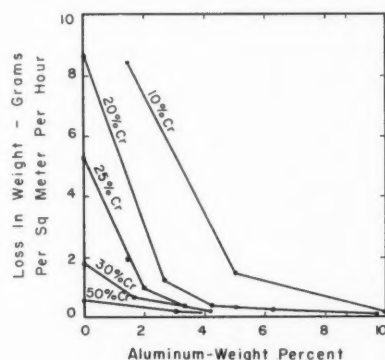
Figure 7—Scaling losses of cast Fe-Cr-Al alloys at 219 F. Duration of tests was 240 hours (from Kornilov[9]).

drop in tensile and yield properties at about 14 percent aluminum is coincident with the formation of the ordered Fe_3Al phase.

Iron-Chromium-Aluminum

Since about 1940, Russian metallurgists have done a great deal of work with the iron-chromium-aluminum system. A partially complete phase diagram at room temperature developed by Kornilov[8] is shown in Figure 5. The region of interest corresponds to chromium contents up to about 30 percent and aluminum contents up to about 12 percent. This region is a single-phase solid solution of iron, chromium, and aluminum. The effects of composition on hot and cold workability are indicated in Figure 6.

The combined effect of chromium and aluminum on oxidation resistance was determined by Kornilov[9] as shown in Figure 7. The results show that the effectiveness of aluminum in reducing scaling losses is much greater than chromium. As shown in these data, a 10 percent chromium-10 percent aluminum alloy is more resistant than a 50 percent chromium alloy.

On the basis of investigations by Kornilov, four types of Fe-Cr-Al alloys were recommended for industrial use as resistance heating elements in the USSR. Typical compositions and properties of these alloys are listed in Table 1. A similar series of alloys are currently in use as resistors in the United States,[10] (see Table 2 for composition and properties).

Oil-Ash Corrosion

The severe corrosion of boiler and heater tubes by ash-forming residues in residual fuel oils has received much attention in the past ten years. A recent review of the oil-ash corrosion problem was presented by Slunder.[11] The results of various studies have established that Na_2SO_4-V_2O_5 mixtures destroy the protective film on the metal by forming molten complex compounds. An accelerated corrosion rate is maintained by the oxygen that is absorbed in the molten mixture. None of the available heat resistant alloys are usefully resistant under severe conditions. However, tests with experimental alloys have shown the beneficial effects of silicon and aluminum as alloying elements.[12]

Iron-chromium-aluminum alloys were tested in various grades of residual fuel oils by the Naval Research Laboratory. Srawley[13] presented data showing that the experimental iron-chromium-aluminum alloys were more resistant than AISI Type 310 under conditions of the test. Three grades of fuel oil were used for the tests and identified as shown in Table 3.

Samples were placed in the exhaust-gas stream of microburners and the temperature was maintained for 100 hours at 1600 F and at 1700 F. The results listed in Table 4 show that the addition of aluminum effectively reduces the corrosion rate below that of Type 310 stainless steel.

The beneficial effects of aluminum were further confirmed by the results of field tests reported by McDowell, Roudebaugh, and Somers.[14] Samples were exposed in the superheater of an oil-fired boiler using Bunker C fuel oil. Racks were suspended in the flue-gas for 648 hours. The temperature ranged from 1220 F to 1560 F. As shown in Table 5, Type 406 containing 12 percent chromium and 4 percent aluminum was more resistant than the other materials tested.

Laboratory tests were made to establish the effect of aluminum in a series of binary iron-aluminum alloys. The samples were dipped in a paste containing 6 moles of V_2O_5 for each mole of Na_2SO_4. The coated specimens were suspended in a small electric furnace for 100 hours at three different temperatures: 1300 F, 1350 F, and 1425 F. The results shown in Table 6 indicate that the amount of aluminum may be critical. The chemical compositions of the samples are shown in Table 7. At both

Figure 8—Scaling rates of Fe-Al alloys in 100 percent hydrogen sulfide. Test duration was 50 hours.

TABLE 3—Grades of Fuel Oil Used in Tests

Fuel	Sulfur, Percent	Vanadium, Percent	Sodium, Percent
Average Navy Special......	1.83	0.017	0.0022
High Vanadium...	2.48	0.0198	0.0007
High Sodium.	1.20	0.0008	0.0283
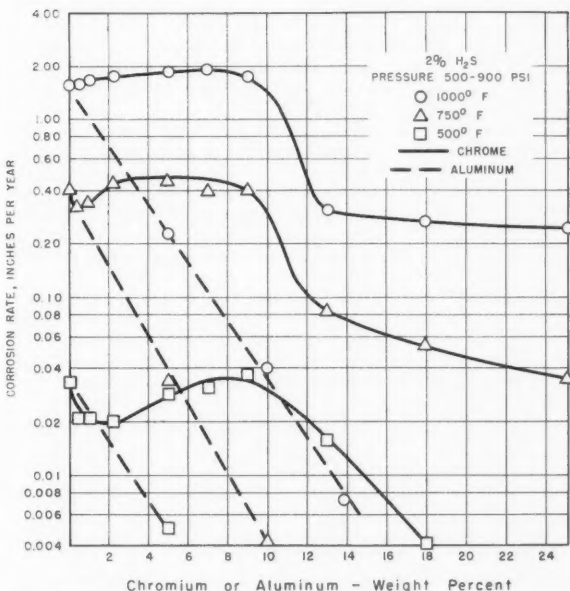
Figure 9—Comparison of chromium steels with Fe-Al alloys at various temperatures. Test duration: 24 hours.
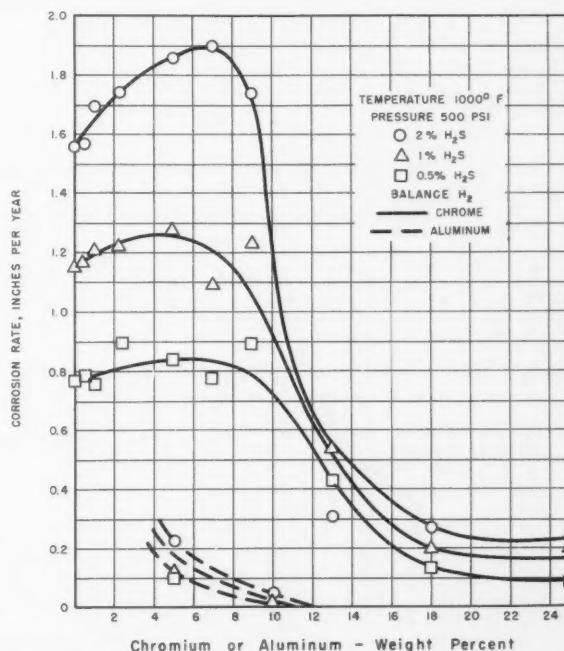
Figure 10—Comparison of chromium steels with Fe-Al alloys at various concentrations of hydrogen sulfide. Test duration: 24 hours.
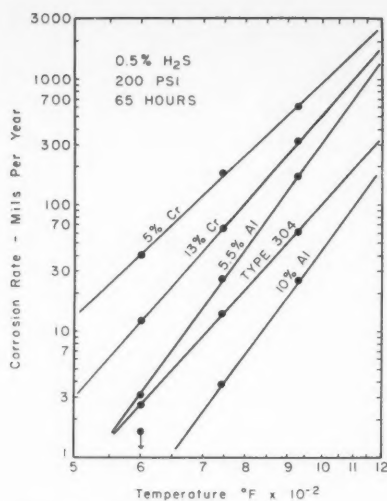
Figure 11—Effect of temperature on the corrosion rates of conventional alloys and iron-aluminum alloys.

1300 F and 1350 F, the 10 percent aluminum alloy is more resistant than the alloy containing 6 percent and 15 percent aluminum. In view of the crude and severe conditions of the test, this may or may not be a reliable trend.

Hydrogen-Sulfide Corrosion

The rapid expansion of catalytic reforming and catalytic desulfurizing created new and severe corrosion problems associated with hydrogen sulfide at elevated temperatures. A considerable amount of test work[15, 16, 17] has shown that austenitic stainless steels and aluminized steels are usefully resistant to sulfidation by hydrogen sulfide. The excellent resistance of aluminized steels prompted a series of tests to establish minimum alloy requirements in iron-aluminum and iron-aluminum-chromium alloys when exposed to hydrogen-hydrogen sulfide atmospheres.

Very little work has been reported concerning the resistance of iron-aluminum alloys in hydrogen sulfide. In 1938, Naumann[18] presented the data shown in Figure 8 illustrating the effect of aluminum as an alloying element in 100 percent hydrogen sulfide at various temperatures. According to Naumann's results, the corrosion rate goes through a maximum between 1 and 2 percent aluminum. At 7 percent aluminum, the corrosion rate is less than carbon steel, particularly at 1112 F.

Preliminary short-term tests, 24 hours duration, were made in the authors' laboratory to compare a series of iron-aluminum alloys with commercial grades of chromium-molybdenum and chromium-nickel steels. The analysis of the steels is shown in Table 7. The tests were made in a hydrogen atmosphere containing 2 percent hydrogen sulfide at 500, 750, and 1000 F. The results shown in Figure 9, indicate that an iron-aluminum alloy containing about 6 percent aluminum is roughly equivalent in resistance to an 18 Cr-8 Ni stainless steel. The points corresponding to 18 and 25 percent chromium in Figures 9 and 10 are 18 Cr-8 Ni and 25 Cr-20 Ni steels. Figure 10 shows the effect of varying the hydrogen sulfide concentration at 1000 F, based on 24-hour tests. Figure 11 shows a comparison at various temperatures between commercial alloys and two iron-aluminum alloys containing 5.5 and 10 percent aluminum. Type 304 is more resistant than the 5.5 percent aluminum alloy and less resistant than the 10 percent aluminum alloy under the 65-hour test conditions.

A series of iron-aluminum and iron-chromium-aluminum alloys were exposed to a hydrogen atmosphere containing 1 percent hydrogen sulfide at 850 F for 200 hours. The total pressure of the system was 200 psi. These test conditions are comparable to conditions encountered in many commercial desulfurizing units. As shown in Figure 12, the addition of chromium decreases the amount of alumium required to reduce the cor-

rosion rate to an acceptable level. For example, an alloy containing 9 percent chromium and 4 percent aluminum is equivalent in corrosion resistance to an iron-aluminum alloy containing 8 percent aluminum. The 9 Cr-4 Al alloy would probably be easier to produce and fabricate than the higher aluminum alloy.

Backensto[19] reported the results of exposing a 12 chromium-4 aluminum alloy, AISI Type 406, to a hydrogen atmosphere containing 1.5 percent hydrogen sulfide at 750 F for 730 hours. The corrosion rates tabulated in Table 8 show that Type 406 is more resistant than the chromium-nickel alloys exposed to the same conditions. Although Type 406 is used primarily as a resistor, the typical mechanical properties listed in Table 2 are adequate for consideration in other applications. However, before these alloys are used in a critical service, considerably more work must be done on weldability and the effect of long-term exposure at elevated temperature on structural changes.

Because of density differences, it is better to compare the effectiveness of chromium and aluminum on an atomic percent basis rather than a weight percent basis. Figure 13 shows a plot of corrosion rates versus the atomic percent of alloying element. Using this criteria, the data show that the sharp drop in corrosion rates occurs in the 9 to 12 atomic percent range for both chromium and aluminum. For atomic percentages above 12 percent, aluminum appears to be more effective than chromium and less effective below 9 atomic percent.

Summary

The transition from experimental heats of iron-aluminum and iron-aluminum-chromium into commercial alloys has been hampered by difficulties in producing wrought products. Results of the accelerated research programs currently underway have eliminated many of the deterrents and today these alloys are under consideration for use in compressors, aircraft, automobile engines, furnaces, and various plant processing equipment.

The addition of aluminum to high chromium alloys markedly improves resistance to oil-ash corrosion. The Navy is considering the use of iron-chromium-aluminum castings for tube supports. The results of this application will be of considerable interest to the petroleum industry.

A limited amount of testing indicates that iron-aluminum and iron-chromium-

TABLE 4—Weight Losses in Microburner Tests (Srawley)[13]

	Weight Loss in Milligrams Per Square Inch Per 100 Hours					
	1600 F Tests			1700 F Tests		
Material	Navy Special	High Vanadium	High Sodium	Navy Special	High Vanadium	High Sodium
24.8 Cr—3.4 Al......	137	150	23	89	235	18
25.2 Cr—5.0 Al......	154	161	5	97	180	26
23.5 Cr—9.4 Al......	50	194	5	117	75	2
AISI 310...........	920	464	60	952	367	81
60 Cr—40 Ni........	195	204	84	372	280	60

TABLE 5—Corrosion Rates Obtained on Samples Exposed in Boiler Burning Bunker C Fuel Oil[14]

Material—AISI Type	Corrosion Rate, Inches per Year
406 (12 Cr-4 Al)..........	0.108
446 (28 Cr).............	0.189
302 (18 Cr-8 Ni).........	0.406
410 (12 Cr).............	0.555
321 (18 Cr-8 Ni-Ti).......	0.690
431 (17 Cr-2 Ni).........	0.906

Temperature Range: 1050—1560 F
Duration of Test: 648 Hours.

TABLE 6—Corrosion Tests of Iron-Aluminum Alloys in Oil Ash Residue—100 Hour Tests

Material	CORROSION RATE—INCHES PER YEAR		
	1300 F**	1350 F*	1425 F**
Type 304 (18 Cr-9 Ni).....................	0.21	0.78	0.62
18 Cr-13 Ni-2.2 Si........................	0.45	1.18	2.05
Type 310 (25 Cr-20 Ni)....................	0.26	0.84	1.01
94 Fe-5.5 Al............................	0.33	0.49	0.79
90 Fe-10 Al............................	0.03	0.14	1.09
85 Fe-15 Al............................	0.26	0.81	1.27

* Samples dipped in paste containing 6 moles of V_2O_5 to 1 mole of Na_2SO_4 at start of test and again after 60 hours.
** Samples dipped in paste only at start of test.
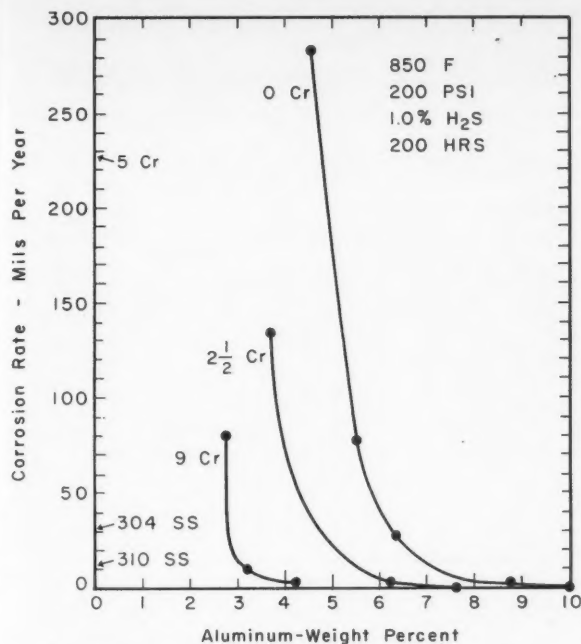
Figure 12—Corrosion rates of Fe-Cr-Al alloys in hydrogen sulfide.
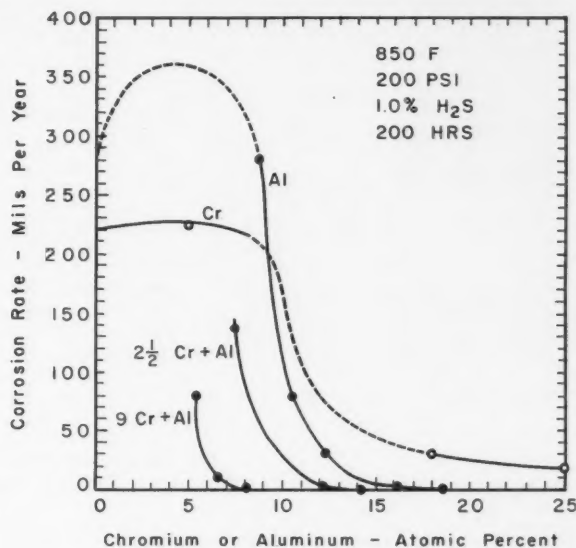
Figure 13—Corrosion rate versus atomic percent of chromium and aluminum.

TABLE 7—Chemical Analysis of Metals Tested

Metal	ELEMENT, PERCENT							
	C	Mn	Si	Cr	Ni	Mo	Al	Cb
Carbon and Alloy Steels								
A-285-C	0.20	0.38	0.02	....	0.01	....	....	....
A-301-A	0.18	0.55	0.25	0.78	....	0.45	....	....
A-301-B	0.15	0.47	0.23	1.11	....	0.48	....	....
A-335-P22	0.10	0.45	0.29	2.18	....	0.95	....	....
A-357-52T	0.08	0.55	0.60	5.04	....	0.47	....	....
A-335-P7	0.09	0.53	0.79	6.78	0.17	0.51	....	....
A-335-P9	0.15	0.45	0.35	8.70	....	0.95	....	....
Stainless Steels								
405D	0.06	0.40	0.33	13.25	0.38	....	0.24	....
302B	0.08	1.67	2.22	18.08	12.88	0.09	....	....
304H	0.08	1.19	0.44	18.60	9.04	....	....	....
347A	0.08	1.60	0.76	17.67	10.72	....	....	0.91
310A	0.08	1.38	1.21	25.37	19.71	....	....	0.01
Iron-Aluminum Alloys:								
5.5 Al	0.07	NA*	NA	....	....	....	5.53	....
10 Al	0.03	NA	NA	....	....	....	9.85	....
Alfenol	0.04	NA	NA	....	....	....	14.42	....
Thermenol	NA	NA	NA	....	....	3.07	14.81	....
X-1	0.13	NA	NA	....	....	....	4.43	....
X-2	0.30	NA	NA	....	....	....	6.26	....
X-3	0.13	NA	NA	....	....	....	8.75	....
Iron-Chromium-Aluminum Alloys:								
X-4	0.13	NA	NA	2.64	....	0.25	3.71	....
X-5	0.27	NA	NA	2.39	....	0.25	6.27	....
X-6	0.38	NA	NA	2.68	....	0.25	7.65	....
X-7	0.15	NA	NA	8.66	....	....	2.76	....
X-8	0.22	NA	NA	9.32	....	....	3.21	....
X-9	0.25	NA	NA	9.44	....	....	4.27	....

* NA—Not analyzed.

aluminum alloys are highly resistant to hydrogen sulfide at elevated temperatures. In many applications, these alloys could replace austenitic stainless steels.

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TABLE 8—Corrosion Rates of Fe-Cr-Ni and Fe-Cr-Al in H₂S at Elevated Temperature (Backensto)[19]

Alloy	Composition	Mils Per Year
Type 304	18 Cr–9 Ni	7.8
Type 347	18 Cr–11 Ni	6.4
Type 309	22 Cr–14 Ni	4.9
Incoloy	21 Cr–34 Ni	2.9
Inco 804	30 Cr–42 Ni	5.0
Inconel	15 Cr–78 Ni	10.1
Type 406	12 Cr–4 Al	Nil
Croloy 20–2 Al	20 Cr–2 Al	3.0

Temperature:	750 F
Hydrogen Pressure:	485 psig
H₂S Concentration in H₂	1.5 percent
Length of Test:	730 hours

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DISCUSSION

Question by Robert W. Manuel, Socony Mobil Oil Co., New York, N. Y.:

Do not all of the Fe-Cr-Al and Fe-Al alloys become brittle upon long exposure at 700-1000 F even if originally ductile?

Reply by Richard B. Setterlund:

We have not seen data on the effect of long term exposure on the Fe-Cr-Al or Fe-Al alloys in this temperature range. We would expect that alloys with over 15-percent chromium would become embrittled. In order to establish if brittleness occurs at the 13-percent chromium level we are presently conducting a test on a heat of Type 406 at 885 F. After 1000 hours we find that the alloy is still ductile. The results of the test are shown below.

Analysis: C .07, Mn .33, Si .65, Cr 13.59, Al 4.02

Sample Size: 2-inch x 1-inch x .092-inch.

Heat Treatment: 1 hr 2000 F, AC, 2 hr 1400 F, WQ

Time at 885 F	Average Hardness
0 hrs	92.1 Rb
2 hrs	92.7 Rb
24 hrs	93.0 Rb
140 hrs	93.0 Rb
300 hrs	93.0 Rb
1000 hrs	94.5 Rb

All samples given 180 degree guided bend without signs of cracking.

Vol. 17

shown

Si .65,

x .092-

F, AC,

ge
ess
Rb
Rb
Rb
Rb
Rb
Rb

guided

Acid Corrosion Inhibition
With Secondary Acetylenic Alcohols*

By JOHN G. FUNKHOUSER

About
the
Author

JOHN G. FUNKHOUSER is an applications chemist at the Technical Sales Laboratory of Air Reduction Chemical Co., Bound Brook, N.J. He received a BA degree in Chemistry from Amherst College in 1956, joining Air Reduction immediately thereafter. His fields of interest in applications and development work include corrosion, latex paints, chlorinated hydrocarbon stabilization, solvents, and defoaming. Mr. Funkhouser is a member of ACS.

Introduction

THE HIGHLY corrosive nature of aqueous mineral acids on most metals necessitates some degree of protection in order to achieve economic maintenance and operation of equipment, minimum loss of chemical products, and maximum safety conditions. Acid corrosion inhibitors provide such protection in many industral operatons such as oil well acidizing, acid pickling, and acid cleaning.

Products that retard corrosion of metals in acid environments do not belong to a single class of chemical compounds. Inorganic salts and complex ions, organic amines, quaternary ammonium salts, nitrogen-containing heterocyclic and aliphatic compounds, mercaptans, and thioureas are all employed to some extent in industry. However, the trend towards higher temperatures and pressures in the use of aqueous mineral acids requires the development of better and more stable corrosion inhibitors.

Early German work reported that certain acetylenic alcohols and glycols are acid corrosion inhibitors[1]. This paper deals with the evaluation and performance of some secondary acetylenic alcohols which have recently become commercially available.

Alcohols are generally divided into three classes: primary, secondary, and tertiary. A secondary alcohol has the hydroxyl group attached to a secondary carbon atom, that is, one which is attached to two other carbon atoms. Figure 1 shows the general chemical structures of the three types of acetylenic alcohols. The symbol, R, represents a short chain linear or branched alkyl group.

Experimental

To obtain comparative performance data in the laboratory, a standard weight-loss screening test was employed. The metals tested were hot-rolled mild steel, SAE 1010-1015; oil well tubing, 2⅜ inch O.D.; and aluminum alloy, 24S[1]. All metal samples were cut into 1 inch

★ Submitted for publication September 21, 1960. A paper presented at a meeting of the South Central Region, National Association of Corrosion Engineers, Tulsa, Oklahoma, October 25-27, 1960.

[1] 93.4 percent Al, 4.5 percent Cu, 1.5 percent Mg, 0.6 percent Mn.

x 2 inch x 1/16 inch coupons except the oil well tubing. It was cut into 2 inch lengths and quartered longitudinally. The coupons were cleaned with solvent, and, if necessary, pickled in inhibited 15 percent HCl until all mill scale was removed. Acetone was used for rinsing prior to weighing.

The inhibitor concentration was expressed as weight percent based on total weight of acid solution. Coupons were immersed in a designated weight of the preheated acid solution for periods from 5 hours to 90 days. Upon removal, each coupon was washed with soap and water using a toothbrush to remove adhering corrosion products, and rinsed with acetone before weighing. The percent protection based on the weight-loss relative to a blank or coupon in uninhibited acid was calculated from the formula:

$$\text{Percent protection} = \frac{\text{wt loss blank coupon} - \text{wt loss inhibited coupon}}{\text{wt loss blank coupon}} \times 100$$

The development of corrosion data at 250 F using P-105 oil well tubing was accomplished by means of a modified pressure cooker. Bottles containing 200 gm of inhibited 15 percent HCl were placed in a pressure cooker partially filled with boiling water. Allowing 20 minutes for the acid solutions to come to temperature, the coupons were immersed and a glass plate was placed over the mouth of each bottle. After closing the pressure cooker, a temperature of 247-252 F was maintained at 15-17 pounds per square inch gauge pressure. The apparatus was vented after 4 hours immersion, and the coupons were removed, washed and weighed.

In this study, the corrosion rate expressed in mils penetration per year (mpy) served as a criterion of protection.

$$\text{Corrosion rate (mpy)} = \frac{534 \, W}{DAT}$$

W = weight loss, mg.
D = density metal, g/cc.
A = surface area, sq. in.
T = immersion time, hr.

Abstract

The mechanism of corrosion and the currently accepted theory of corrosion inhibition with respect to acetylenic alcohols is briefly considered. Several laboratory test methods for evaluating corrosion inhibitors are given. Factors affecting corrosion and corrosion control include type and concentration of corrosive medium, type of metal to be protected, temperature, amount of oxygen and impurities present, testing methods, and type and concentration of inhibitor.

Secondary acetylenic alcohols (e.g., hexynol, and ethyl octynol) function as corrosion inhibitors specifically in aqueous mineral acids. Extensive laboratory data are presented on the prevention of metallic corrosion in aqueous mineral acids with secondary acetylenic alcohols. Such data point to industrial application in oil well acidizing (protection of API oil well tubing P-105 in 15 percent HCl at 250 F), acid cleaning (protection of aluminum and mild steel in 5 and 15 percent HCl at 104 and 150 F respectively) and acid pickling (protection of mild steel in 15 percent HCl at 150 F and 15 percent H₂SO₄ at 187 F). Studies also indicate that hexynol may be used as a component in an inhibitor mixture to prevent corrosion of mild steel by concentrated grades of H₃PO₄   5.8.2, 4.3.2

Discussion of Results

The data in Table 1 serve to compare the performance of several secondary acetylenic alcohols with three commercial corrosion inhibitors in a mild steel-hydrochloric acid system. An immersion time of 17 hours in 15 percent HCl at 180 F was used to evaluate both inhibitor performance and stability. Note that 4-methyl-1-pentyn-3-ol was not stable enough to provide protection although

TABLE 1—Corrosion Inhibition of Mild Steel in 15 Percent HCl at 180 F*

Corrosion Inhibitor	Percent Protection	Corrosion Rate, mpy
None		14,200
4-Methyl-1-pentyn-3-ol	9	12,800
1-Hexyn-3-ol	99	150
4-Ethyl-1-Octyn-3ol	99	180
1-Propyn-3-ol	95	780
Commercial Inhibitor A**	77	3,310
Commercial Inhibitor B***	98	320

* Inhibitor concentration 0.2 wt. percent; 100 gm acid; 17 hr. immersion time.
** Inhibitor A is a mixture of high boiling alkyl-substituted pyridines.
*** Inhibitor B is a proprietary inhibitor based on a dehydroabietyl amine derivative.

PRIMARY ACETYLENIC ALCOHOL

```
    H
    |
HC≡C-C-H
    |
    OH
```

SECONDARY ACETYLENIC ALCOHOL

```
    H
    |
HC≡C-C-R
    |
    OH
```

TERTIARY ACETYLENIC ALCOHOL

```
    CH₃
    |
HC≡C-C-R
    |
    OH
```

Figure 1—Chemical structure of acetylenic alcohols.

INHIBITOR (S)	CONC. WT. %	CORROSION RATE, MPY X 10^{-3}
HEXYNOL	1.0	16.6
ETHYL OCTYNOL POLYOXYETHYLENE (4-5 MOLES)	1.0	35.0
PROPARGYL ALCOHOL	1.0	23.0
COMMERCIAL INHIBITOR A[A]	1.0 / 0.5	1.7 / 4.0
COMMERCIAL INHIBITOR B[B]	1.0	8.9
HEXYNOL ETHYL OCTYNOL	0.25/0.25	35.2
HEXYNOL COMMERCIAL INHIBITOR A[A]	0.5/0.5 / 0.25/0.25	0.8 / 1.1
HEXYNOL COMMERCIAL INHIBITOR C[C]	0.5/0.5 / 0.25/0.25	1.3 / 11.3
HEXYNOL COMMERCIAL INHIBITOR D[D]	0.5/0.5	5.4
HEXYNOL POLYOXYETHYLENE (12) TRIDECYL ALCOHOL	0.25/0.25	21.0
HEXYNOL POLYOXYETHYLENE (15) NONYL PHENOL	0.25/0.25	17.6
HEXYNOL COMMERCIAL INHIBITOR E[E]	0.25/0.25	32.2
HEXYNOL LOW MOL.WT. POLYAMIDE RESIN	0.25/0.25	22.0
HEXYNOL FATTY ACID DIAMINE	0.5/0.5	9.7
HEXYNOL FATTY ACID AMMONIUM CHLORIDE	0.5/0.5	19.7

200 G ACID   5 HRS IMMERSION TIME

A. PROPRIETARY INHIBITOR RECOMMENDED FOR HIGH TEMPERATURE OIL WELL ACIDIZING.
B. PROPRIETARY INHIBITOR RECOMMENDED FOR OIL WELL ACIDIZING.
C. A MIXTURE OF HIGH-BOILING ALKYL SUBSTITUTED PYRIDINES.
D. PROPRIETARY INHIBITOR RECOMMENDED FOR HYDROCHLORIC ACID.
E. A MIXTURE OF DEHYDROABIETYL AMINE AND POLYOXYETHYLENE (5) DEHYDROABIETYL AMINE.

Figure 2—Corrosion inhibition of P-105 oil well tubing in 15 percent HCl at 250 F.

PERCENT PROTECTION

	0	20	40	60	80	100

HEXYNOL
ETHYL OCTYNOL
4-METHYL-1-PENTYN-3-OL
ETHYNYL CYCLOHEXANOL
PROPARGYL ALCOHOL

KEY
5 HR. IMMERSION TIME
24 HR. IMMERSION TIME
100 G ACID
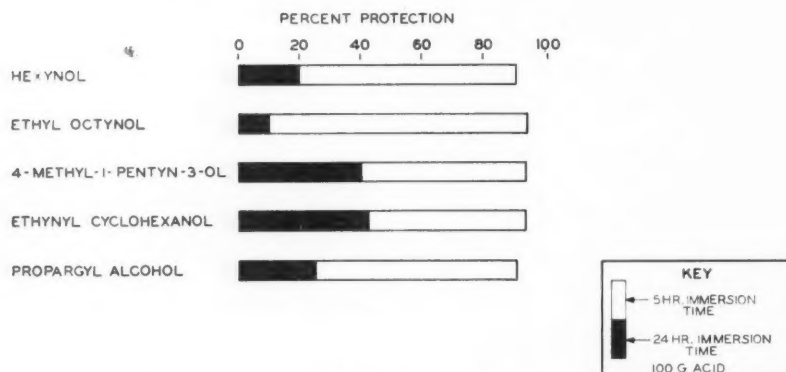
Figure 3—Corrosion inhibition of mild steel in 15 percent H$_2$SO$_4$ at 187 F.

TABLE 2—Corrosion Inhibition of Mild Steel in Concentrated Phosphoric Acid at 76 F*

	Corrosion Rate, mpy		
Concentration and Grade of H$_3$PO$_4$	Mixture A	Mixture B	Blank**
85 Percent CP Grade	0.06	0.23	207
85 Percent Commercial, "White"	0.22	0.32	244
95 Percent Fertilizer, "Green"	3.2	3.9	274

* Inhibitor concentration 0.1 wt. percent; 100 gm acid; 90 day immersion time.
** Corrosion rate based on 24 hrs. immersion time due to rapid corrosion and formation of protective coating on coupon.

it is a good inhibitor at lower temperatures (see page 113).

Preliminary evaluation of hexynol and ethyl octynol as corrosion inhibitors for oil well acidizing applications was conducted in 15 percent HCl at 250 F with API designated P-105 high-tensile oil well tubing. Data are presented in Figure 2. No control or uninhibited acid system was run due to the violent reaction between iron and hydrochloric acid at this temperature. Ethyl octynol proved too insoluble to evaluate in the simple system employed. Although hexynol appears to be better than propargyl alcohol, it did not provide adequate protection at this temperature. Therefore, mixtures of hexynol with other compounds, mostly commercial corrosion inhibitors, were tested. Many of these compounds were amines with which hexynol appears to react in the presence of hydrochloric acid to form an amine-acetylenic alcohol reaction product. Many such products have a high potential utility as corrosion inhibitors not only in high temperature hydrochloric acid but other aqueous mineral acids as well.

Corrosion inhibition with secondary acetylenic alcohols has been described for steel-hydrochloric acid systems. The degree of protection offered by secondary acetylenic alcohols for mild steel in sulfuric acid, phosphoric acid, and sulfamic acid is presented below.

Figures 3, 4 and 5 illustrate the percent protection exhibited by three secondary acetylenic alcohols for mild steel in 15 percent H$_2$SO$_4$, 15 percent H$_3$PO$_4$, and 10 percent sulfamic acid at elevated temperatures. Ethynyl cyclohexanol and propargyl alcohol were included for comparison.

In 15 percent H$_2$SO$_4$ (Figure 3) all products tested exhibited good protection for a 5 hour immersion time (unshaded column); however, protection over 24 hours immersion (shaded column) was poor for all the acetylenic alcohols because of inhibitor degradation. In 15 percent H$_3$PO$_4$ (Figure 4) several of the acetylenic alcohols gave fair protection, but again, were unstable over 24 hours. In 10 percent sulfamic acid (Figure 5) stability over 24 hours was again inadequate with the exception of ethynyl cyclohexanol.

Although corrosion inhibition has been stressed in dilute acid solutions, some interesting results have been obtained on the protection of mild steel in several grades of concentrated phosphoric acid. Table 2 indicates the protection afforded by two inhibitor mixtures designated as Mixture A and Mixture B. Mixture A contains hexynol and a proprietary nitrogen-containing inhibitor. Mixture B consists of hexynol, a tridecyl alcohol polyoxyethlene surfactant, and potassium iodide. The tests were performed at room temperature for an immersion time of 90 days.

The corrosion rate in inhibited phosphoric acid increases as the impurities in the acid increase; however, a corrosion rate of less than 5 mpy in all grades of concentrated phosphoric acid may be considered satisfactory[2]. The remarkable stability and synergistic inhibiting prop-
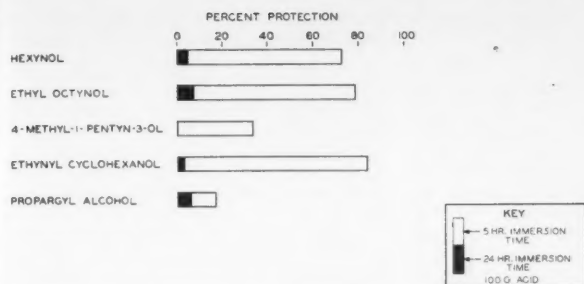
Figure 4—Corrosion inhibition of mild steel in 15 percent H₃PO₄ at 187 F.

Figure 5—Corrosion inhibition of mild steel in 10 percent sulfamic acid at 150 F.

Figure 6—Corrosion inhibition of aluminum alloy 24S in 5 percent HCl at 104 F.
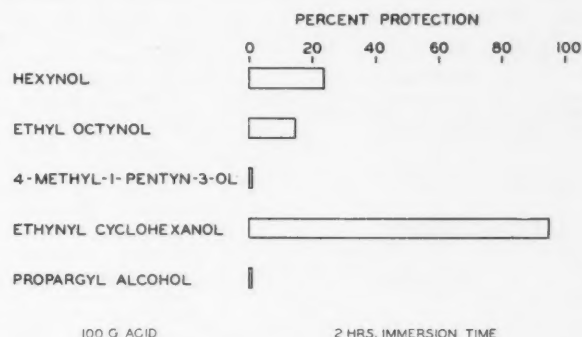
Figure 7—Corrosion inhibition of aluminum alloy 24S in 15 percent H₃PO₄ at 150 F.

erties of hexynol suggests its application in the protection of shipping containers, storage tanks, and operating equipment for commercial grades of phosphoric acid.

The protection of aluminum in 5 percent HCl and 15 percent H₃PO₄ at elevated temperatures is indicated in Figures 6 and 7. Immersion times of only a few hours were used in these tests due to the extreme reactivity of aluminum in aqueous mineral acids.

In 5 percent HCl (Figure 6) hexynol, 4-methyl-1-pentyn-3-ol and ethynyl cyclohexanol exhibited greater than 90 percent protection. In 15 percent H₃PO₄ (Figure 7) only ethynyl cyclohexanol showed potential utility as a corrosion inhibitor under the test conditions.

Laboratory work so far has indicated that acetylenic alcohols do not inhibit the corrosion of mild steel in sour (hydrogen sulfide contaminated) brines, gasoline contaminated with water, and organic acids. No tests have been performed to evaluate secondary acetylenic alcohols as corrosion inhibitors under refinery conditions due to their apparent selectivity and the difficulty in simulating actual refining conditions under which corrosion inhibitors must provide protection.

Factors Influencing Corrosion and Corrosion Inhibition

Variables Encountered in Testing Methods

Ideally, the laboratory evaluation of corrosion inhibitors should be performed under conditions duplicating those of the proposed industrial application. This of course is difficult to achieve due to the complexity of industrial conditions and the wide variety of environments. To obtain meaningful results, and to provide

at least a partial basis for their interpretation in relation to practical conditions, it is necessary to know some of the variables which influence the corrosion rates obtained on a laboratory scale.

Corrosion rate calculated from weight-loss measurements will vary according to the ratio of acid volume to exposed metal. If small amounts of acid are employed for long immersion times, the rate of corrosion will decrease as the strength of the acid is depleted by its reaction with the metal. However, in acid solutions containing effective inhibitors, increasingly greater protection is obtained as the ratio of the volume of solution to the area of the exposed metal is increased. This seemly anomalous result is more easily understood by considering that in a larger solution volume, a larger absolute amount of inhibitor is available for adsorption per unit area of metal surface.

The immersion time of the metal coupon in acid solutions must take into account inhibitor stability in the acid medium. Many compounds exhibit excellent protection for short durations, but will fail over extended periods of time.

The selection and preparation of metal coupons will influence corrosion test results. An unpolished steel surface corrodes many times more rapidly than a polished surface.[3] Corrosion generally occurs more rapidly at the edge surfaces of the coupon due to intergranular attack; hence a high ratio of minor to major surface area will give unrealistic results. Accordingly, care should be taken not to use coupons which are too thick.

The location of the coupon in the acid solution is important. If a high percentage of the metal surface is in close
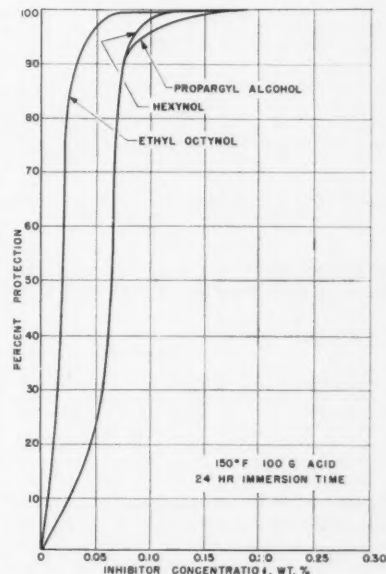
Figure 8—The protection of mild steel in 15 percent HCl as a function of inhibitor concentration.

TABLE 3—Corrosion of Oil Well Tubing in 15 Percent HCl at 150 F*

Oil Well Tubing, API Designation	Corrosion Rate, mpy	
	Blank	0.1% Hexynol
H-40	26,900	36
N-80	18,200	87
P-105	13,200	170
J-55	13,200	135

* 400 gm acid; 5 hr. immersion time.
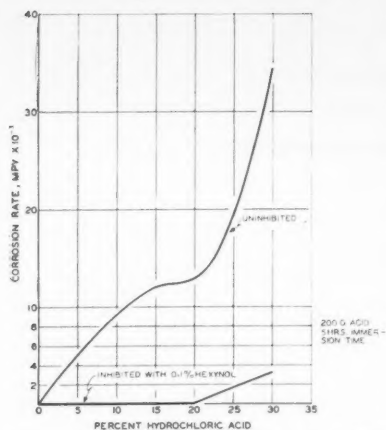
Figure 9—Effect of hydrochloric acid concentration on the corrosion rate of mild steel at 150 F.
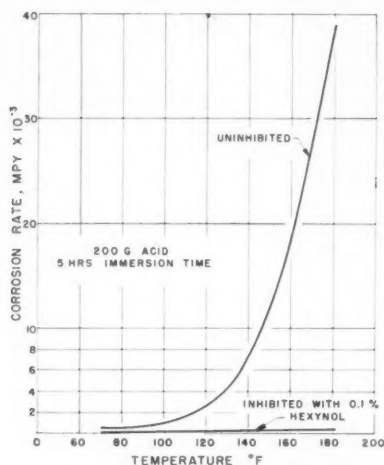
Figure 10—Effect of temperature on the corrosion rate of mild steel in 15 percent HCl.

TABLE 4—Effect of Oxygen on Corrosion Rate of Mild Steel in 15 Percent HCl at 76 F*

	Corrosion Rate, mpy	
Description	Blank	0.1% Hexynol
Oxygen-Free......	317	7
Oxygen Present....	399	9

* 100 gm acid; 5 hr. immersion time.

TABLE 5—Effect of Contaminants on the Corrosion Rate of Mild Steel in 15 Percent Inhibited HCl at 150 F*

Contaminant	Percent Protection**	Corrosion Rate, mpy
None............	99.4	71
0.50 Wt. % Fe++ (as FeCl2)......	98.7	151
0.50 Wt. % Fe+++ (as FeCl3)......	95.5	540
0.50 Wt. % Cu++ (as CuCl2)......	88.5	1360
0.50 Wt. % Cr+++ (as CrCl3)......	99.3	89
0.05 Wt. % H2S...	58.9	6400

* Inhibitor concentration 0.1 wt. percent hexynol; 100 gm acid; 5 hr. immersion time.
** Based on weight loss of unhibited contaminated solutions.

contact with the glass container, concentration cell corrosion may occur[4].

Inhibitor concentration is a critical consideration in the comparison of corrosion inhibitors. If too little inhibitor is used, there will be no evidence of protection; too high a concentration may mask the difference in performance of different inhibitors. Figure 8 shows the effect of inhibitor concentration on corrosion rate of mild steel in 15 percent HCl.

Solubility of inhibitors can be important if the compound is not thoroughly dispersed or solubilized. As the metal coupon is immersed, it will pass through a surface layer of inhibitor which can physically adsorb on the coupon providing greater than normal protection during complete immersion. This condition may give rise to misleading results in laboratory studies.

The acids most generally used in oil well acidizing, acid cleaning and acid pickling are hydrochloric or muriatic, sulfuric, phosphoric, and sulfamic acid. The degree of corrosion is dependent upon the acid environment. For example, in 15 percent aqueous solutions, mild steel corrodes least in phosphoric acid and more in hydrochloric than in sulfuric acid. Concentration of the acid also is a factor influencing corrosion rate. Figure 9 illustrates the corrosive effect of different concentrations of hydrochloric acid on mild steel. The increasing corrosion rate in the inhibited acid at concentrations above 20 percent HCl is explained by the partial degradation of inhibitor; yet protection is still above 90 percent.

Metal

Corrosion rates are governed by the metal composition. Alloys of iron with certain elements such as silicon, molybdenum, nickel, tungsten decrease the corrosion rate of the metal in acid solutions. On the other hand, some components in iron or steel accelerate corrosion. For instance, the corrosion rate and difficulty in inhibiting corrosion increase with increasing carbon content of steel. The variation in corrosion rates of several different types of API oil well tubing in 15 percent HCl may be seen from Table 3. Hexynol inhibits the corrosion of all four types of tubing despite their differences in corrosivity in uninhibited acid.

Temperature

The temperature of the corrosive medium has a marked influence on corrosion rate. Figure 10 illustrates the rapid acceleration of corrosion in an uninhibited acid solution as the temperature rises from 70 F to 180 F. In contrast, inhibited acid exhibits only a slight increase in corrosion rate, even at 180 F.

Oxygen

In an air-free system, polarization can occur due to an insulating blanket of hydrogen gas adsorbed at the cathode. The presence of air or oxygen may prevent polarization by reacting with hydrogen ions to form water, thus current flow

is resumed and corrosion proceeds. In acid media, the following reaction occurs:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
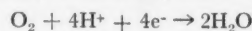
The greater the supply of oxygen to the metal surface, the faster the reaction occurs. Table 4 illustrates the effect of oxygen on the corrosion rate of mild steel in 15 percent HCl. The degree of protection in the inhibited acid is not affected by the presence of oxygen.

Impurities

Impurities of foreign matter occluded in the metal surface increase corrosion and are conducive to pitting. Contaminants in the acid may also accelerate corrosion and pitting. Generally, oxidizing cations such as Fe^{+++}, Fe^{++}, Cu^{++}, and Cr^{+++} cause accelerated corrosion and pitting in aqueous solutions of hydrochloric acid. Fe^{+++} ($FeCl_3$) especially accelerates the corrosion of steel in hydrochloric acid. Hydrogen sulfide is a particularly severe corrodent in acid solutions. Some ferrous sulfide is present in most refinery and oil-producing equipment due to continual handling of hydrogen sulfide contaminated hydrocarbons and brines. Acid cleaning liberates the gas which in turn reacts with iron to form ferrous sulfide again.

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

$$H_2S + Fe \rightarrow FeS + H_2$$

Hydrogen embrittlement may also occur when the hydrogen evolved from the above reaction remains in monoatomic form and penetrates into the lattice of steel. The hydrogen then forms hydrogen gas at inclusions in the steel causing blistering and cracking at that point. Uncontaminated acid solutions may also cause hydrogen embrittlement while acetylenic alcohols retard this phenomenon[5, 6, 7].

Table 5 illustrates the effect of several contaminants on the corrosion rate of mild steel in 15 percent HCl inhibited with 0.1 percent hexynol. Protection is decreased by the presence of contaminants. Hydrogen sulfide caused inhibitor break-down. No pitting occurred on any of the inhibited steel coupons although pitting was prevalent in acid solutions contaminated with Fe^{+++}, Fe^{++}, and Cu^{++}.

Mechanism of Corrosion and Corrosion Inhibition

In an attempt to understand how an acetylenic alcohol functions as a corrosion inhibitor, it may be helpful to consider the general mechanism of corrosion.

Corrosion of metals in aqueous solutions is generally considered to be electrochemical in nature. Figure 11 schematically represents a corrosion cell in an acid environment. The reactions for corrosion of iron in acid are as follows:

$$Fe - 2e^- \rightarrow Fe^{++} \text{ (Oxidation at anode)}$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (Reduction at cathode)}$$
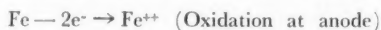
If the flow of current is reduced at either the anode or cathode due to polarization, then dissolution of the metal is correspondingly reduced. Corrosion inhibitors

generally function as polarizers by adsorption at the anode, cathode, or over the entire surface of the metal.

The triple bond of an acetylenic alcohol acts as a focal point of adsorption of the molecule to the metal surface. It has been postulated that chemisorption occurs by the sharing of a pair of electrons from the triple bond with anodic sites on the metal surface.[8] The degree of protection exhibited by acetylenic alcohols is directly related to the extent of chemisorption or the strength of the inhibitor-metal bond. This, in turn, is a function of inhibitor solubility and stability in the acid, and is also influenced by substituent groups attached to the basic acetylenic alcohol molecule.

The data illustrated in Figure 12 indicate the radical differences in protection that can occur with different acetylenic alcohols in a mild steel-hydrochloric acid system. Generally, primary and secondary acetylenic alcohols provide good protection; tertiary alcohols are less effective. Increasing molecular weight of the secondary acetylenic alcohols increases protection, although branching also affects protection. As molecular weight increases, however, solubility in aqueous systems decreases; e.g., hexynol is approximately 2.5 percent soluble whereas ethyl octynol is less than 0.05 percent soluble in 15 percent HCl at 25 C. The primary acetylenic alcohol studied provides nearly as good protection as hexynol and ethyl octynol at 150 F, but it is not as stable at temperatures above 150 F.

It is interesting to note the relationship of the size of inhibitor molecules to the extent of surface coverage or adsorption. Assuming adsorption occurs at the triple bond, the molecules will lie almost horizontally on the surface of the metal. The surface area of metal covered by one hexynol molecule is approximately twice that covered by the smaller propargyl alcohol molecule. In other words, there are twice as many propargyl alcohol molecules adsorbed per unit area as hexynol molecules. Since both compounds are effective inhibitors in hydrochloric acid at 150 F, on a mole for mole basis, hexynol provides protection to twice the area that propargyl alcohol would effectively inhibit. On an equal weight basis, hexynol would theoretically inhibit 13 percent more surface area.

Conclusions

The secondary acetylenic alcohols, 1-hexyn-3-ol and 4-ethyl-1-octyn-3-ol, are effective as corrosion inhibitors in specific
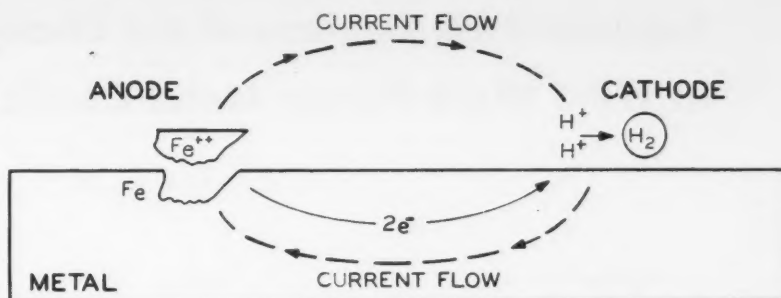
Figure 11—Schematic corrosion cell of iron in acid environment.

Figure 12—The effect of the structure of acetylenic alcohols on the protection of mild steel in 15 percent HCl at 150 F.

systems. The selectivity of these alcohols makes them useful in aqueous mineral acids used in acid cleaning, oil well acidizing, and acid pickling.

Synergistic combinations of secondary acetylenic alcohols with other corrosion inhibitors and reaction products of secondary acetylenic alcohols improve their performance and broaden their fields of application.

Acknowledgement

The author acknowledges data provided by J. W. Kennette, and expresses his appreciation to C. O. Herman and Dr. C. E. Blades for their advice and cooperation.

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Any discussion of this article not published above will appear in December, 1961 issue.

Suggested Mechanisms of the Changes With Time
In WP-1 Wash Primer Metal Conditioning Composition*

By EDWARD R. ALLEN

Introduction

PROCESSES OF baffling complexity are often developed through skillful empirical research to a point where they find important applications. Extension of fundamental research to such developments is logical. Such an approach normally passes through a pioneer stage during which the reactions involved are isolated and their relevancy to the process indicated. The next step is the formulation of a tentative hypothesis of the mechanism of the changes involved with a view to developing this into a coherent guiding theory, the purpose of which is to render the basic research still more effective. It is submitted that the basic research work sponsored by the Office of Naval Research[1] during 1953-56 on wash primers, has produced findings which justify an attempt at formulating such a hypothesis.

The term 'wash primer' designates a specific product that combines the properties of the familiar inhibitive wash coat or metal conditioner with the properties of the conventional anti-corrosive primer.[1] Wash primers, developed through research in the laboratories of the Bakelite Company under an agreement with the National Defense Research Committee during World War II, were announced to the public in 1947.[1] The reactive, the reacted and the non-reactive types which were developed have been described by Whiting.[1] The most important of these by far is the reactive type designated as WP-1 or MIL-P-15328 and covered in a basic patent issued to Whiting and Wangner[2] and assigned to the Secretary of the Navy. The distinctive quality of this composition so applied as to form thin (0.5 mil) films, is its altogether unusual adhesion to metals, and the fact that most coating compositions adhere very strongly to it. It is therefore classed as a metal pre-treatment or metal conditioner as contrasted to a conventional formula.

Most of the Office of Naval Research Program was directed toward the study of the behavior and mechanism of the action of WP-1, although important observations were made on the reacted type by Professor Eirich and associates (see page 116).

In its most familiar form WP-1 is a two package system, the one an alcoholic solution of phosphoric acid, the other a dispersion of zinc tetroxychromate (ZTC), in an alcoholic solution of the resin, polyvinylbutyral, (PVB). The two are mixed just prior to use, whereupon

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★ Submitted for publication August 4, 1960.

[1] Research Contracts NONR 404(06) and 404(07); NONR1126(00); also Naval Research Laboratory.

Abstract

A brief outline is given of the history of wash primers with emphasis on laboratory research. A mechanism is postulated to explain the loss of adhesion with time of WP-1. Topics discussed include phase rule studies of zinc tetraoxychromate, intrinsic viscosities of recovered polymers, reactions involving formation of phosphorus-chromius-resin complex, deposition of tertiary zinc phosphate on metal, and modifications made in WP-1. Several organic structural formulae are included.   5.4.5

a reaction—or series of reactions—set in. This is why the term reactive comes to be used. The pot life of the mixture is short, usually stated to be eight hours.

The deterioration (i.e., loss of adhesion with time of this product), has been the subject of discussion, debate, experimentation and research since its disclosure to the public. While the reactions involved are by no means fully understood, the above suggested theoretical explanation may be attempted.

It has generally been recognized that a phosphorus-chromium-resin complex is formed which is, in some unexplained way, vital to the proper functioning of the composition. It has been pointed out[3] that oxidizable alcohols are transformed to aldehydes (or ketones) with corresponding reduction of chromium (VI) to chromium (III), following which the latter combines with the resin. The resulting complex is positively charged, and the suggestion was that the phosphate was associated with it, probably as in the formula indicated here as Figure 1.

Rosenbloom[4] showed clearly that the presence of oxidizable alcohol, necessary for formation of the complex, is in turn vital to the proper functioning of the composition, and also concluded that
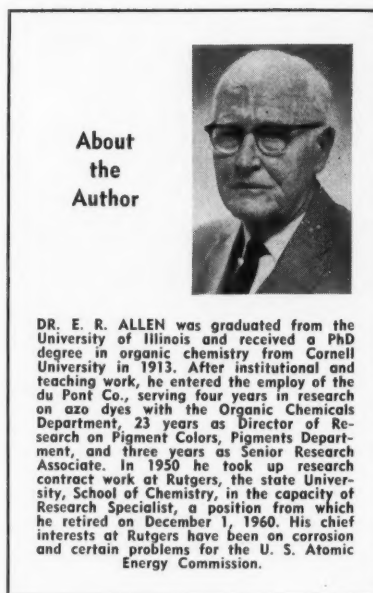
About the Author

DR. E. R. ALLEN was graduated from the University of Illinois and received a PhD degree in organic chemistry from Cornell University in 1913. After institutional and teaching work, he entered the employ of the du Pont Co., serving four years in research on azo dyes with the Organic Chemicals Department, 23 years as Director of Research on Pigment Colors, Pigments Department, and three years as Senior Research Associate. In 1950 he took up research contract work at Rutgers, the state University, School of Chemistry, in the capacity of Research Specialist, a position from which he retired on December 1, 1960. His chief interests at Rutgers have been on corrosion and certain problems for the U. S. Atomic Energy Commission.

phosphoric acid has no direct effect on the resin. This latter point is of interest since it is at variance with the idea held by some students of the process that the decrease in phosphoric acid with time was due, in part at least, to esterification of the resin.

Recent Investigations

In 1953, research of a basic nature, under the above mentioned sponsorship of the Office of Naval Research was
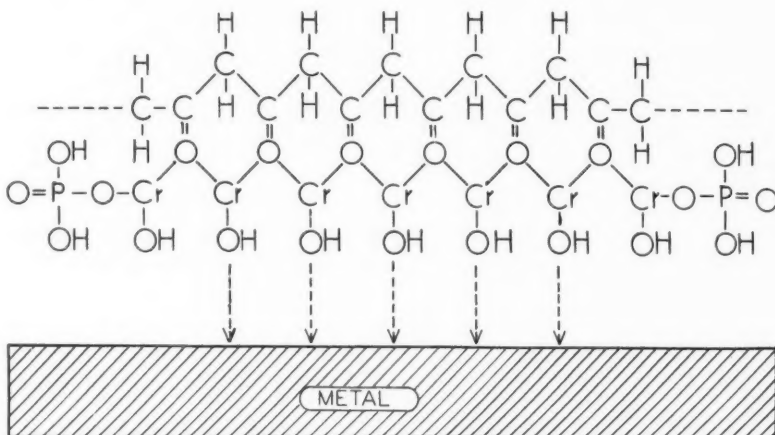
Figure 1—Early idea of formula for phosphorus-chromium-resin complex.
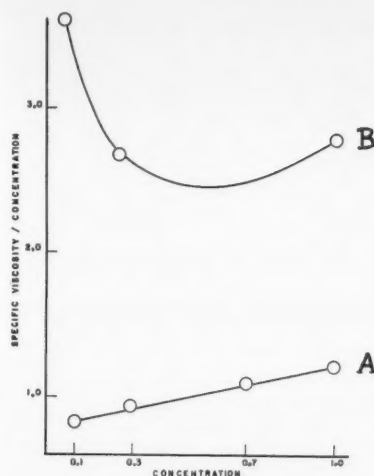
Figure 2—Graphic determination of intrinsic viscosities of PVB (A) and of phosphorylated PVB (B).

Figure 3—Graphic determination of intrinsic viscosities of recovered polymers.

TABLE 1—Shift in Equilibrium of Reversible Acteal Cleavage Reaction

Reflex Time, Hour	Aldehyde Liberated, Percent Total
0.8. . . . . .control run.	7.3
0.5. . . . . .plus CrCl₃.	25.7

instituted by Barnes, Allen, et al, at Rutgers, by Eirich et al, at the Polytechnic of Brooklyn, and by Bloom et al, at the Naval Research Laboratory.

Program at Rutgers

Woodward, Allen and Anderson[5] showed, by a phase rule study, that ZTC, $5ZnO \cdot CrO_3 \cdot 4H_2O$, was most likely a solid solution rather than a chemical compound since the composition of the solid phase can vary over a considerable range without evidence of a break in properties. Broadly, basicity varies inversely as the solubility. The product, ZTC, shows a low solubility, is highly basic and therefore readily reactive with phosphoric acid. This is in harmony with the findings at the Fort Belvoir works (see page 116) which recognized that zinc tetroxychromate as the sole inhibitive pigment is unsuitable because of its reactivity. This phase rule study gives a clearer explanation of Leisy's disclosure[6] than this worker's viewpoint that ZTC is a chemical individual. The phase rule interpretation is that the product is distinctive in that it is a saturated solid solution. Leisy's X-ray work has been checked[7] with the supplemental information that a higher percentage of ZnO (i.e., toward the ZnO apex of the triangular diagram), reveals clearly ZnO patterns—in this case the presence of free zinc oxide. The point corresponding to $5ZnO \cdot CrO_3 \cdot 4H_2O$ coincides with the theoretical quite well on the diagram, and it is reasonable to believe that more refined work would show an unmistakable agreement. On the other hand, passing in the other direction on the diagram there is a large area of continuously varying compositions (i.e., increasing CrO_3 solubilities and decreasing basici-

ties). Such findings would certainly be of interest in following up on the important observations at the Fort Belvoir Laboratories.
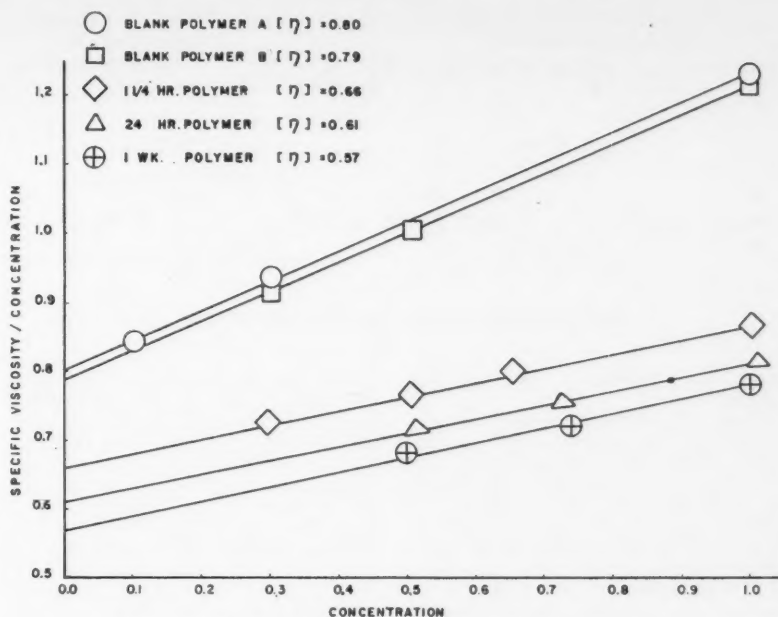
The evidence is that the commercial product is reasonably constant in composition. Still, in the Fort Belvoir work some variations were encountered, and Bloom showed by X-ray diffraction that the composition can vary considerably under different methods of preparation.

Ruigh and Allen[8] showed in a preliminary study that the formation of phosphoric esters of PVB was improbable, but it remained for Barnes[9] to clarify this point. This resin, recovered after the action of phosphoric acid, showed a viscosity curve essentially identical with that of the original material. In contrast, a phosphoric acid ester of the resin, prepared by accepted synthetic procedures, showed the characteristic viscosity curve of a polyelectrolyte. This is shown in Figure 2.

This method of using intrinsic viscosity determinations to distinguish between a neutral polymer and a polyelectrolyte—a polymer carrying ionizable groups—is an elegant procedure widely recognized in modern polymer chemistry. The principles involved were briefly stated by Hirshfield and Allen.[10] The question therefore of the esterification of PVB by phosphoric acid under conditions existing in the WP-1 composition is therefore unequivocally answered in the negative.

Barnes states the important conclusion "No evidence has been found to indicate that there is, in ethanol, any esterification of the phosphoric acid by the hydroxyl groups of the polymer."[9]

Barnes also found that the phosphoric acid *does* give rise, through a reversible reaction, to some cleavage of the acetal linkages of the resin. This point was established unequivocally by the recovery

and identification, as its 2:4 dinitrophenylhydrazone, of the liberated aldehyde.

A third very important point was also established by Barnes. He found that in the presence of salts of chromium (III), the equilibrium of the reversible acetal cleavage reaction is shifted strongly in favor of aldehyde formation as shown in Table 1.

The important point here is that the hydrolytic action of the phosphoric acid is unmistakably accelerated by the presence of chromium (III) salts, presumably through chelation.

Hirshfield and Allen[10] developed a method for recovering the resin from the WP-1 mixture[12] and also made important observations on the rate of disappearance of the phosphoric acid in the mix. Using exactly the same technique for determining viscosity as that employed by Barnes, it was found that the intrinsic viscosity of the resin from the one hour charge of WP-1 (i.e., undeteriorated), showed a marked drop in intrinsic viscosity as compared with the original resin. It was found also that a slow decrease in this property continued with time. There was no indication of a break that could be correlated with the point of objectionable deterioration. As seen from Figure 3, no evidence of polyelectrolyte formation is revealed. The indications were that free phosphoric acid decreases rapidly, so that only the equivalent of 50 percent of the amount originally added is present at the end of one hour. However, the disappearance of phosphoric acid could not be correlated with the deterioration of the mix.

In order to facilitate the study of the fate of the inorganic materials, chromates, phosphates, and zinc, Allen[11], et al modified the Hirshfield and Allen technique so that the WP-1 mix was resolved

$$\overset{\text{3}}{\underset{\text{3}}{PVBut}} + Cr\ PO_4 + H_3\ PO_4 \longrightarrow$$

"PVBut" stands here for the complete resin.

$$\overset{\text{3}}{\underset{\text{3}}{PVBut}}\ ..\ Cr^{3+}\ .\ \begin{bmatrix} HPO_4^= \\ H_2PO_4^- \end{bmatrix} \rightleftharpoons \overset{\text{3}}{\underset{\text{3}}{PVBut}}\ .\ Cr^{3+}\ .\ \begin{bmatrix} HPO_4^= \\ HPO_4^= \end{bmatrix}^- + H^+$$
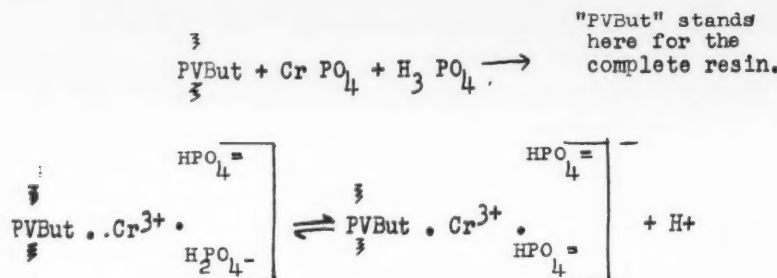
Figure 4—Postulated structures formed in reacted wash primer.

Figure 5—Viscosity curve of isolated complex. Curve shows that the complex is a polyelectrolyte.

into resin, pigmentary material and aqueous extract.

From this different method of approach (i.e., the analyses of the aqueous extracts and of the pigmentary residues), the results were tentatively interpreted to mean that only acid phosphates of zinc are present in the aqueous extract at the end of the short period of one hour. Also there were indications that these acid phosphates of zinc gradually go over to the insoluble tertiary product so that in the deteriorated charge very little acidic material remains. The rapid reaction of the phosphoric acid with the highly basic ZTC is amply confirmed, and the idea that the main decrease in phosphoric acid is due to esterification of the resin is no longer tenable. Again no attempt was made to correlate these changes with loss of adhesion.

Analyses showed that, in accordance with the general viewpoint, reduction of chromium (VI) does occur, but that, contrary to statements often made, it is not completely consumed even in deteriorated charges. Soxhlet extracted recovered pigmentary materials showed in all cases the presence of large amounts of chromate chromium. Loss of adhesion therefore can *not* be attributed to lack of chromium (VI).

The exact fate of the chromium (III) is uncertain. The presence of the expected chromium phosphate could not be established with certainty. The acetic acid extraction of the pigmentary material removed, as expected, the chromates of zinc, leaving a copious residue of fluffy gray-green material. It was shown to contain considerable organic matter (resin) and to contain both chromium and phosphorus, but the analyses did not approach the values for chromium phosphate. Conceivably it is a mixture of chromium phosphate and a phosphorus-chromium-resin complex, insoluble in alcohol, entirely different therefore from the bright green complex referred to above, and viewed as of vital importance. Hitherto unreported by other workers it comprises about 10 percent of the pigmentary material from fresh charges, and rises to over twice this in the deteriorated mixes. For want of a better appellative, it is designated as the "mixture-complex."

Exploratory analytical work on random samples of recovered resin established the presence of chromium and of phosphorus in small but determinable amounts. While it was not absolutely

certain these were chemical combinations, and while it has not been established whether it is or is not a polyelectrolyte, the observation that the t-butyl alcohol[2] solutions of the recovered resin showed increasing greenness with time suggested the presence of the phosphorus-chromium-resin complex. By a series of solutions and reprecipitations a small amount of a clear bright green resin was separated from the main portion of the resin recovered from a deteriorated charge; the same technique applied to a counterpart from a fresh charge yielded a resin fraction only faintly tinted with green. On the assumption that the greenish material is the phosphorus-chromium-resin complex, the inference is that this material is produced in small and gradually increasing amounts in WP-1.

Program at the Polymer Institute of the Polytechnic Institute of Brooklyn

Eirich[13] and associates studied the reacted type of wash primer, Bakelite XL-5367[14]. This product is prepared by adding a concentrated aqueous solution (A) of chromic acid to an approximate 10 percent solution of phosphoric acid in acetone, (B), then adding this mixture to an approximate 6 percent solution of PVB in ethanol (C) after which this second mixture is further diluted with butanol to form the final preparation (D). While this preparation is quite different from WP-1, there is the possibility that observations on it have at least a suggestive value to WP-1. Eirich showed that the chromium (VI) is completely reduced in this particular composition and it was concluded that the chromic ions are quantitatively complexed by the resin, which acts as a polydentate ligand and that the phosphate ions are in turn held to the complexed (chelated) chromic ions. The structure shown in Figure 4 is postulated in this connection.

The isolated complex gave the viscosity curve, Figure 5, showing unequivocally that it *is* a polyelectrolyte. The logical interpretation of this is that the ionizable phosphate residue is attached to the complex.

It is interesting to note the resemblance of this modern formula to the one suggested by the pioneers depicted in Figure 1.

The molar ratio of $CrO_3:H_3PO_4:PVB$ (-unit) is given as approximately 0.5:

(2) Used in preparing solutions for freeze-drying.
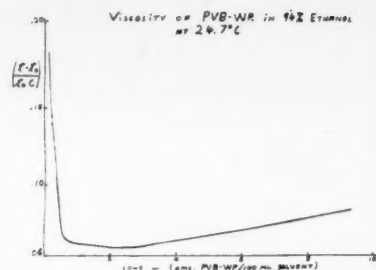
1:10, which means a relatively small fraction of the resin is complexed.

Eirich also suggested that the chromium phosphate is completely complexed with the PVB immediately after formation.[15]

Program at the Naval Research Laboratory

Kruger and Bloom[16] showed that tertiary zinc phosphate is deposited on the metal. The acid phosphates were not identified, nor was chromium phosphate. The evidence on this last point was not considered conclusive since chromic phosphate does not show characteristic X-ray patterns. The zinc phosphate was viewed as important as a film former because its atomic radius approximates that of iron; therefore $(FeZn)_3(PO_4)_2 4H_2O$ was visualized as attaching to the iron surface. Attention was also called to Machu's work relative to the sealing of holes in the phosphate film by chromate ions, and the suggestion made that WP-1 may so function by supplying chromate ions for this purpose.

Program at the Engineer Center, U. S. Army, Fort Belvoir, Va.

This program of applied research, carried out concurrently with the Office of Naval Research work, involved evaluating a large number of modifications of WP-1. From this work it was concluded that the reduction of reactivity was in order. The revision made was that one-half of the ZTC in WP-1 be replaced by strontium chromate, and that the phosphoric acid be markedly reduced. In WP-1 the preferred ratio of PVB:ZTC:phosphoric acid is 2:2:1[1], whereas in the Fort Belvoir version the corresponding relations are 2:2:0.6. This resulted in an increase in stability with the result that a one package product is now used as Army Specification MIL-C-1504.

The recognition of the high reactivity resulting from the liberal use of phosphoric acid and ZTC in WP-1 compositions is certainly in harmony with the Rutgers observations. These materials react violently in aqueous systems, and, as would be expected, more slowly but appreciably in alcoholic systems. The reactions between the phosphoric acid and the resin, accelerated by the presence of chromium (III) salts as observed by Barnes, is quite possibly significant and would be curtailed by the adjustments recommended in the Fort Belvoir work.

$$RCH_2\text{-}CH \quad CH\text{-}R^1 \qquad H_3PO_4 \qquad \longrightarrow \qquad RCH_2\text{-}CH \quad CH\text{-}R^1 \quad + C_3H_7CHO$$

$$H_2O$$
$$CrPO_4$$
$$Cr_2(HPO_4)$$
$$Cr(H_2PO_4)_3$$

$$C_3H_7 \qquad\qquad\qquad\qquad\qquad\qquad CrH_2PO_4 \quad ?$$
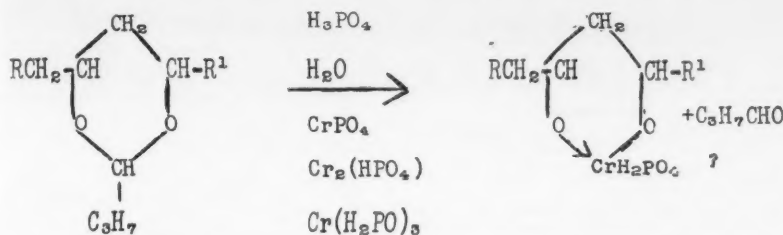
Figure 6—Reactions involved in the formation of phosphorus-chromium-resin complex.

TABLE 2—After Treatment of Zinc Phosphate Layer on Steel

After Treatment	Wt. Loss gm/m²/day
None	0.284
Sodium Chromate	0.184
Aluminum Sulfate	0.524
Aluminum Sulfate mixed with ACP Rodine III	0.075
Aluminum Sulfate mixed with Di-o-tolythiourea	0.057
Aluminum Sulfate mixed with Dibenzyl sulfoxide	0.038

At any rate this work does show that the study of the WP-1 formulation is a fruitful problem.

Proposed Tentative Mechanism of the Reactions in WP-1

Reference is first made to the observation of Hirshfield and Allen relative to the marked drop in intrinsic viscosity of the resin on incorporation into the WP-1 process. This phenomenon was not investigated in detail on the assumption that this change was not pertinent to the interpretation of deterioration since it was shown by the resin from the one hour (undeteriorated) charge. From some exploratory work, which has since been informally reported to the writer the suggestion has arisen that the WP-1 composition passes through an optimum earlier than has been generally suspected. This is an important point if true and suggests studying the gap shown in Figure 3 between the "blanks" and the recovered polymers.

Rosenbloom's previously outlined explanation that the reason for the vital necessity of an oxidizable alcohol is to render possible the information of the phosphorus-chromium-resin complex is in harmony with this recent research work. It is now visualized that the change occurs in the resin to cause a drop in its intrinsic viscosity (Hirshfield and Allen) after or accompanying which the following reactions proceed: In the presence of phosphoric acid, through the oxidation of the alcoholic hydroxyl groups and corresponding chromate reduction there results a mixture of phosphoric acid, the phosphates and the acid phosphates of chromium (and probably of zinc). This mixture then reacts with the resin under acetal cleavage (Barnes) to form a phosphorus-chromium-resin complex.

Figure 6 gives the simplest concept of this set of reactions.

The phosphate radical instead of being completely reacted with chromium, may be partially acidic, or zinc may replace some of the chromium. Chelation with zinc, while theoretically possible, is deemed unlikely. In any case a product possessing the type of structure shown is a polyelectrolyte. That the chelation is with the hydroxyl groups liberated through the acetal cleavage, rather than through the free hydroxyl groups of the resin, harmonizes with the identification by Barnes of the recovered aldehyde hydrazone and also by the increase in liberated aldehyde accompanying the addition of $CrCl_3$.

The above structural formula for the complex, admittedly over-simplified, shows a Cr:P ratio of 1:1, whereas the structure suggested by Rosenbloom (Figure 1) shows 7:2, and that by Eirich in Figure 4 corresponds to 0:5:1. Not enough analytical data have been obtained as yet to determine which of the proposed formulas, if any, is correct. Eirich's product was obtained, as stated above, from a composition quite different from WP-1; the formula and ratios were proposed to account for observed abnormal conductivities and the possibility that there is adsorption of phosphate ions on to the resin complex. In the face of these uncertainties the formula in Figure 6 is proposed pending further information.

It should not be overlooked that this set of reactions implies an increase with time of the hydrolytic cleavage of the acetal groups. It implies also a corresponding increase in the formation of butyraldehyde, some acetaldehyde (or corresponding acids), as well as the increase in the amount of complex formed. Whether this chelation of chromium (III), with retention of phosphate substantially quantitative, takes place in WP-1, as shown by Eirich in the related system, is still uncertain. Such a reaction, however, would assist in explaining some of the experimental observations made on WP-1. However, from the meagre data obtained by Allen et al, on the qualitative separation of a green complex from the resins recovered from WP-1 it is tentatively concluded that a small amount of such a complex is formed in this composition, and that this amount slowly increases with time.

In accepting the thesis that the phosphorus-chromium-resin complex is vital to the performance of WP-1 the burden is assumed of explaining how a very small, really minute, amount of this product can so function. This complex does not form instantaneously, yet the evidence is that it is effective. There is the extreme case in commercial practice of the spray gun co-mixing of the components,[17] therefore only minute amounts of complex are possible in such short time intervals. Whether such practice is functionally fully equal to the normal procedure is not relevant at this point since the thesis is supported that minute amounts of the complex are effective. That such amounts function by direct action on the film forming properties of PVB in WP-1 is difficult to visualize.

The most probable explanation appears to lie in the influence of this method on

the traditional problem of the crystallinity[3] and porosity of the phosphate layer. Machu,[18] in addition to determining the action of chromates in sealing the defects in the phosphate layer, found much more pronounced actions through after treatment with other materials such as insoluble phosphates and some organic compounds of relatively high molecular weights. To cite one experiment from extended researches on this phenomenon, in the after treatment of a zinc phosphate layer on steel, the data given in Table 2 were reported.

It is postulated that the role of the phosphorus-chrominum-resin or bright green complex lies in some such action, or possibly in modifying the crystallinity of the zinc phosphate.[4] It is not necessary, theoretically, in this hypothesis for this high molecular weight sealer or modifier to be a polyelectrolyte. It is conceivable, however, that the ionizable product would be more effective than is a neutral polymer.

The significance of the larger amount of the bright green complex in a deteriorated charge is at present uncertain. While it is possible that it is an adverse factor, the amount even here appears to be so small that in the author's judgment it is more likely that it is a reaction product produced concomitantly beyond the minute requirements of the above postulated favorable functions.

Whether the resin itself is concerned in the deterioration seems rather doubtful, although this cannot be safely disregarded without more pertinent evidence.

Until evidence to the contrary is available the assumption is that the fluffy gray-green mixture-complex formed in appreciable amounts, exerts an unfavorable effect on adhesion. The tertiary zinc phosphate may act similarly. That is, the formation with time of excessive amounts of either or both of these products could contribute to loss of adhesion. Adverse effects from excessive deposits of zinc phosphate in the coating of metals are recognized.[19]

In the light of the Office of Naval Research work, and of that at Fort Belvoir, the factors therefore which appear to contribute to the loss of adhesion in WP-1, are: (1) decomposition products from the resin through acetal cleavage, (i.e., butyraldehyde and butyric acid), (2) the

[3] Bloom established by X-ray determinations that crystalline $Zn_3(PO_4)_2 \cdot 4H_2O$ is deposited on the metal in the WP-1 processing.

[4] Some attempts have been made to define distinctive inhibitive properties of chelate compounds, but this concept is still in the formative stage.

presence of excessive amounts of the mixture-complex, (3) the over, or improper, production of insoluble zinc phosphate, and (4) overconsumption of the acid phosphates. It is possible that through this last action the pH of the mix becomes too high to permit the etching of the metal which does take place, although the vital importance of this point is still uncertain. Reduction in reactivity therefore suggests itself as an important step in overcoming these sources of failure. The modification originating in the Fort Belvoir development harmonizes with this idea.

Summary

Summarizing, it is in order to emphasize that recent research work has made a good start in pin pointing the effective reactions which take place in the very important and intricate WP-1 mix. Using the above postulated tentative mechanism as a guide the further study of the process can now proceed with definitely higher

efficiency. The problem, including refining of this tentative mechanism, is therefore viewed as an inviting field for research.

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Unity of Anaerobic and Aerobic
Iron Corrosion Process in the Soil*

*By Dr. C. A. H. von WOLZOGEN KUHR**

CHAPTER 1
Historical Introduction

PREVIOUS INVESTIGATIONS[1] with regard to iron corrosion in general date from the latter half of the 18th century. These are characterized by a certain one-sidedness, as only corrosion in the presence of oxygen from the air or so-called aerobic corrosion was taken into consideration. Investigations instituted in the Netherlands in 1922, the results of which were first published in 1923[2] have since then been considerably extended. They have shown that iron can also be attacked without coming into contact with oxygen from the air, so-called anaerobic corrosion. Owing to this fact the study of iron corrosion has entered into an entirely new phase. A Corrosion Committee was set up in The Hague in 1931 "Stichting voor Materiaalonderzoek" (Research Institute for Materials) whose task it was to make a systematic study of the corrosion of iron pipelines due to influences of the soil. As early as 1935 the Committee could summarize the first results of its work in a report which was published as Communication No. 10.[3]

The author of this treatise gives the following results of the iron corrosion research, partly as an extract from an article published in 1934[4] about the graphitization of cast iron, the gist of which was included in the above-mentioned Communication No. 10, and partly as a continuation of the study of iron corrosion made by him and his collaborator L. S. van der Vlugt in the laboratory of the Provincial Water Works of North Holland.

The investigations into iron corrosion with the exclusion of oxygen from the air, instituted in the Netherlands, were pursued by England in 1935, while France also took up this work in 1936. Outside Europe the latest research work in iron corrosion with regard to the anaerobic form of corrosion has been carried on in America since 1922.

The growing interest in the problem of iron corrosion due to the influences of the soil in the various countries is comprehensible, as, owing to the extension of iron pipelines in the ground in behalf of industrial enterprises, the loss caused by iron corrosion when the pipes are insufficiently protected or the insulation is damaged during their transport has also greatly increased year by year. It is clear that, by tracing the cause of iron corrosion, the means are being

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Abstract

This paper on the unity of the anaerobic and aerobic iron corrosion process in soil was originally presented at the Fourth National Bureau of Standards Soil Corrosion Conference in 1937. It covers such topics as corrosion from an electrochemical point of view, the anaerobic iron corrosion process, iron corrosion by the sulfate reduction process, iron corrosion by carbonic acid reduction process, iron corrosion by nitrate reduction process, iron corrosion due to chemical substances in the soil, and the aerobic iron corrosion process. A statement is made to the effect that the hydrogen acceptor which is invariably present with all forms of iron corrosion considered, constitutes the unity in the anaerobic and aerobic iron corrosion process in the soil.   4.5.1, 6.2.2

sought to prevent as much as possible, if not entirely, the corrosion of the pipelines.

It is remarkable that in some of the cases of corrosion observed the nature of the corrosion was found to differ from ordinary iron corrosion, which cases are at present designated as anaerobic corrosion.

This treatise is intended to give a consideration of the causes of the aggressiveness of the soil with regard to iron, to emphasize, as a general conclusion, the fact that the corrosion processes of iron pipes in the ground, both anaerobic and aerobic, show—besides accidental differences of surroundings and chemism—a remarkable similarity, based on unity.

CHAPTER 2
Corrosion From An Electrochemical Point of View

Of the various theories regarding the corrosion process of metals in general, the electrochemical one has prevailed, so that it is also being applied in the present treatise.

The corrosion of a piece of metallic iron due to the action of a neutral ground moisture acting as electrolyte, by which the iron is anodically dissolved, is represented by the following equation:

$$2 H_2O \rightarrow 2 \overset{.}{H} + 2 OH' \qquad (1)$$

$$Fe + 2 \overset{.}{H} \rightarrow \overset{..}{Fe} + 2 H \qquad (2)$$
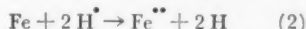
It must be observed here that iron generally shows a distinct tendency to act as a hydrogen donator.

Reaction equation (2) is the equation of the primary iron corrosion in the "corrosion element" in which, according to Nernst,[8] the anodic solution of iron in the electrolyte will continue, if the potential of the iron

$$E_{Fe} = - \frac{0.0002T}{2} \log \frac{P_{Fe}}{p_{Fe..}} \qquad (3)$$

is smaller than the hydrogen potential in regard to the solution:

$$E_H = - \frac{0.0002T}{2} \log \frac{K'_H C_{H2}}{(C_{H.})^2} \qquad (4)$$

In both these formulae E_{Fe} and E_H are the potentials of anode and cathode respectively against the electrolyte, T is the absolute temperature of the solution, P_{Fe} the electrolytic solution pressure of the iron, $p_{Fe..}$ the osmotic pressure of the $Fe^{..}$-ions, K_H a constant, C_{H2} the concentration of the polarizing hydrogen and $C_{H.}$ the concentration of the hydrogen-ions. Owing to the polarizing action of the hydrogen formed at the cathode of the corrosion element, the electro-chemical solution process of the iron would soon cease, due to a fall in the difference of potential between cathode and anode, if no depolarization took place at the cathode, which is explained theoretically by F. Foerster[9] as follows:

For the hydrogen at the cathode:

$$E_H = - 0.415 \text{ Volt.}$$

and for compact iron (measured in a 1 norm. $FeSO_4$ solution):

$$E_{Fe} = - 0.43 \text{ Volt.}$$

from which it follows that the electromotive force of the corrosion element is:

$$E_H - E_{Fe} = + 0.015 \text{ Volt.}$$

To attain equilibrium with the water, hydrogen will be separated off, accompanied by the formation of $Fe^{..}$-ions. These combine with the OH'-ions from (1) to the non-readily soluble $Fe(OH)_2$, one liter of which at 18 C can contain about 2.5×10^{-8} Mol. in solution. Against this OH'-ions solution E_H changes to — 0.58 volt. As, however, E_{Fe} cannot go above — 0.54 volt against this solution and practically adjusts itself in air-free water to — 0.53 volt, the action of the iron on the water must very soon cease and this does in fact occur, the more so if the non-readily soluble hydrates of ferrous oxide formed from $Fe(OH)_2$ deposit as a close film on the iron.

In the literature of the cases of iron corrosion in the soil which have been studied so far, in which only aerobic corrosion has been dealt with, it is only the oxygen from the air, therefore, which acts as depolarizer, so that the depolarization reaction is in this case represented by

$$2H + O \rightarrow H_2O \qquad (5)$$

It has now, however, been ascertained that besides oxygen from the air several other chemical compounds may easily act as depolarizers and the possibility of the anaerobic corrosion of iron is based on this fact.

If a piece of iron of known weight is placed in air-free water containing formaldehyde, sodium oxalate, an oxidizing agent or free sulfur in a stoppered bottle completely full and closed, the iron will be found to have lost weight after some time. Obviously the polarizing hydrogen has been absorbed by the said substances, acting as hydrogen acceptors, so that the iron corrosion can continue according to reaction (2) and the corrosion element remains active.

The greater part of the substances which may cause depolarization do not absorb molecular hydrogen, so that in the iron corrosion process the hydrogen is probably absorbed in an atomic state. This conception is in accordance with the chemical view which ascribes a greater effect to hydrogen in an atomic state than to hydrogen in a molecular state. In this connection it has been taken for granted in the various cases of anaerobic iron corrosion dealt with in Chapter 3, in which microbiological processes take part in the depolarization, that they can bind the atomic hydrogen even more easily than hydrogen in the molecular state.

In what way the condition for the activity of the corrosion element, viz.:

$$E_H > E_{Fe} \qquad (6)$$

is fulfilled in the various iron corrosion processes, is discussed in more detail later in this treatise.

CHAPTER 3

The Anaerobic Iron Corrosion Process

As investigations have shown that compounds, resulting from the anaerobic iron corrosion process in the soil, may later give rise to serious aerobic iron corrosion in case of subsequent aeration of the soil, it is advisable to consider the anaerobic iron corrosion process before the aerobic process.

It might be thought that the corrosion of iron at a considerable depth in a soil showing a neutral reaction and completely shut off from oxygen from the air, accompanied by the development of free hydrogen constitutes a case of anaerobic corrosion. Intentional observations have, however, shown that only iron in a finely divided state forms free hydrogen with an electrolyte, but that in the case of solid pieces of iron, such as dug-in pipe lines (and these only come into consideration from a technical point of view), no development of free hydrogen could be observed under exclusion of air and with a neutral reaction of the ground moisture. If this should occur with solid iron in an *anaerobic* soil the soil conditions deviate from the more general conditions mentioned above and even then the development of free hydrogen would in all probability be so small as to preclude iron corrosion in the technical sense of the word.

The use of finely divided iron as a basis for corrosion tests so as to be able to apply the phenomena thus encountered to the corrosion process of iron pipe lines, is therefore absolutely inadmissible from a technical point of view.

In connection with the anaerobic cor-

rosion of iron pipes in the ground, the following 3 criteria generally apply for characterizing the behavior of iron under anaerobic conditions.

(a) In neutral electrolytes, such as sterile ground water, no free hydrogen is developed, so that no corrosion occurs.

(b) In sterile damp soil and soil suspensions no free hydrogen is formed either, and just as under (a) the iron is not attacked.

(c) The presence of hydrogen acceptors, as which inter alia the substances mentioned in Chapter 2 may serve, is essential, so that they may play the part of depolarizer in the electrochemical iron corrosion process, the result of which is the corrosion of the iron.

Iron Corrosion by the Sulfate Reduction Process

On the basis of the above observations it has become possible to obtain a deeper insight into the anaerobic corrosion process of iron pipe lines. This occurs in soils of a close structure and which are, moreover, rich in water, organic matter and mineral compounds, as is the case with clay and bog soils. In the Netherlands these soils are often encountered in the polder districts, which often lie below sea level. In these low-lying districts, which may often be sodden or even marshy, corroded iron pipes show very clearly the picture of this anaerobic corrosion, which is characterized by the presence of iron sulfide, the amount present in the soil being greater at the place where the iron has corroded than at some distance from it. This iron sulfide, mixed with components of the soil, may also occur as crusts on the iron pipes. This particular sulfide is, as later research has shown, nothing else than the corrosion product of the anaerobic iron corrosion process, characterized by the ferrous condition, i.e. the lowest valency condition that iron can assume in its compounds.

An intensive anaerobic corrosion in the case of steel pipes results in the well-known "pitting," whilst cast iron pipes, which contain about 3.5 percent of carbon, show the so-called graphitization at the spots attacked. This is obviously due to the fact that, with the loss of iron owing to the corrosion process, a soft substance containing iron, rich in carbon or graphite, remains at the deteriorated places, where the pipe wall is greatly weakened. The pipes may give way if they are under a high internal pressure, so that a break may occur in this manner.

In literature the graphitization of cast iron is known under the names of "spongiose" and "iron cancer". The former name refers to the porous structure of the deteriorated cast iron, while the latter refers to the rampant spread of the corrosion.

The presence of iron sulfide as a corrosion product of iron pipes indicates that hydrogen sulfide must be involved somehow in the anaerobic corrosion process. The formation of hydrogen sulfide and iron sulfide in soils under exclusion of oxygen from the air, was ascribed

by M. W. Beijerinck[10] (as early as 1895) to the action of a strictly anaerobic living microbe, called by him Spirillum desulfuricans, and later on called also *Microspira* or *Vibrio desulfuricans,* which is the sole cause of the reduction of sulfates present in the ground to hydrogen sulfide or iron sulfide. He designated this process as sulfate reduction. This microbiological process is only possible if moisture is present and, further, the following conditions are complied with:

(1) Total absence of oxygen from the air.

(2) Presence of assimilable organic compounds and the necessary mineral substances (physiological elements).

(3) The presence of sulfate.

When these conditions are complied with, this process can, therefore, take place even at a very great depth in the soil, as could be demonstrated (according to an aseptic manner of investigation) with reference to samples of clay, originating from a drilling in Bennebroek (a village in North Holland) in 1931 at a depth of 71 meters.

Sulfate reducing spirilla are universal and occur in practically every soil, so that the sulfate reduction process is encountered universally throughout the earth. The sulfate reduction as an exothermic process, by means of the oxidation of the organic food by the combined oxygen from the sulfate, sets free energy, which is utilized physiologically by the sulfate reducing spirilla. In regard to the chemism of the sulfate reduction, J. K. Baars[11] applied the views of A. J. Kluyver and H. J. L. Donker[12]. Both of these investigators had already demonstrated the validity of Wieland's theory concerning the true biological oxidation for various microbiological processes. According to them the living protoplasm constitutes the catalyst having the property of changing the position of the hydrogen in the nutrient medium. Thus any biochemical process is separated into a series of mono-molecular oxido-reductions. In this manner these views were brought into line with more recent chemical experience according to which multimolecular reactions do not occur. In this connection the sulfate reduction chemism, must, according to Baars[13], be given in four successive primary reaction stages, devolving finally to the simple gross equation:

$$H_2SO_4 + 8 H \rightarrow H_2S + 4 H_2O \qquad (7)$$
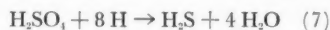
Not only combined hydrogen in the organic food can be oxidized by sulfate oxygen but also free hydrogen, as formerly proved by J. Nikitinsky[14] and later by M. Stephenson and L. H. Strickland[15]. Consequently, it was naturally assumed that with the primary iron corrosion reaction (2) the depolarization reaction (3) is affected by the sulfate oxygen, so that, activated by the biological sulfate reduction process, it acts as hydrogen acceptor. By adding up the equations (1), (2), (5) and (7), and taking into consideration the coefficients, the following reaction scheme of anaerobic iron corrosion with sulfate reduction is obtained:

$$4\,Fe + H_2SO_4 + 2\,H_2O \rightarrow$$
$$3\,Fe(OH)_2 + FeS \qquad (8)$$
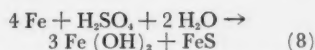
The representation given of the above corrosion process agrees satisfactorily with the results of laboratory tests and facts observed in several cases of anaerobic corrosion of iron pipes in practice; these can be summarized as follows:

(1) In carefully sealed sample bottles filled with ground and water aggressive to iron, in which a solid piece of iron was attacked with formation of iron sulfide, no rise in pressure (besides variations due to fluctuations of the temperature) due to hydrogen being realized according to (2), could be observed by means of a manometric apparatus. If the sample bottles are sterilized the iron corrosion immediately ceases.

In view of the general behavior of iron with anaerobic corrosion, as described in points a, b, and c, as well as the disappearance in the corrosion test of sulfate, which is replaced by iron sulfide, all this leads to the inevitable conclusion that the sulfate reduction process as a biological hydrogen acceptor affects the depolarization in the above corrosion.

(2) A piece of bright iron placed in soil in which the sulfate reduction process had ceased owing to the lack of the required food (sulfate or otherwise) showed no signs of corrosion on its surface in the course of some time. If, however, sulfate reduction is started again by the addition of new food (ground or canal water containing sulfate) corrosion commences on the surface of the iron with darkening due to the formation of iron sulfide. (If the test is made with bright *cast* iron a commencement of corrosion is soon shown at its surface with a grey coloring which is clearly perceptible). This experiment shows that only an active sulfate reduction process can affect the anaerobic corrosion of iron, for a cessation of sulfate reduction is equivalent to the lack of a hydrogen acceptor, which is, according to (c) necessary for the iron corrosion process.

(3) The quotient $\dfrac{Fe}{FeS}$, i.e. the ratio

between the total quantity of corroded iron and the iron found as sulfide in the anaerobic iron corrosion experiments in the laboratory, using ground and canal water, gave values of 2.4 to 3.4, whilst equation (8) gives the value 4. The cause of the difference between the value of the above ratios obtained theoretically and experimentally, is explained by the circumstance that, besides the oxidation of the cathodic hydrogen, oxidation of the hydrogen in the organic food also takes place in the sulfate reduction process, hydrogen sulfide being set free as a product of dissimilation and precipitated in the form of iron sulfide. The Figure 4 will have to be considered as a limit for the experiment in the above solutions. Equation (8) thus corresponding satisfactorily with the experiment, it accordingly represents the iron corrosion process with sulfate reduction, from which it follows that in this case not only iron sulfide but also ferrous hy-

droxide is a product of corrosion. This corrosion is therefore *not caused by hydrogen sulfide*, as in that case free hydrogen would have to develop, and the above ratio would have to be $\dfrac{Fe}{FeS} = 1$, while it is neither one nor the other, as has just been shown.

The remarkable fact that this iron corrosion, which may be very serious, takes place in a practically neutral medium, the reaction of which does not materially change during the process, is accounted for by the circumstance that the corrosion products formed $Fe(OH)_2$ and FeS are of a neutral character.

In considering equations (3) and (4) in connection with the iron corrosion process with sulfate reduction, E_{Fe} will have a maximum negative value in (3), when $p_{Fe..}$ is a minimum. The corrosion products so formed $Fe(OH)_2$ and FeS have a low solubility product, so that the value of $p_{Fe..}$ is inconsiderable and, consequently, E_{Fe} assumes a high negative value. The less negative the hydrogen potential E_H is, the more favorable will be the action of the corrosion element. The reaction of the solution remaining practically neutral in the corrosion process mentioned, as stated before, the vaue of C_H. in (4) may be considered as constant. Consequently, the value of E_H is only dependent on C_{H2} and its negative value is as small as possible when C_{H2} is a minimum too. The value of C_{H2} is kept low by the depolarization which, in the present corrosion process is affected intensively by the sulfate oxygen as a hydrogen acceptor. Condition (6) for the activity of the corrosion element is therefore fulfilled.

Iron Corrosion by Carbonic Acid Reduction Process

In 1906 N. L. Söhngen[16] made the discovery that methane microbes are capable of affecting the formation of methane and water from hydrogen and carbonic acid. This carbonic acid reduction proceeds according to the equation:

$$CO_2 + 8\,H \rightarrow CH_4 + 2\,H_2O \qquad (9)$$

and is an exothermic reaction, in which the energy released serves for the vital functions of the microbes mentioned.

The hydrogen absorption, which, according to his observation, may take place in cultures of cellulose—methane fermentation, he ascribes to this reaction. From the standpoint of anaerobic iron corrosion this carbonic acid reduction process of Söhngen, which takes place completely anaerobically, may therefore bring about iron corrosion as the hydrogen formed according to equation (2) on account of said process oxidizes to water according to reaction (3). Through the agency of the methane microbes the combined oxygen from the carbonic acid consequently acts as hydrogen acceptor in the depolarization in the corrosion element. It could be distinctly proved by means of a laboratory experiment that an iron plaque put into a cellulose-methane fermentation, lost weight for many months owing to the

anaerobic corrosion taking place. By adding chalk the pH of the liquid was maintained at about 7. As Söhngen[17] observed that sulfate reduction takes place very readily in cellulose-methane fermentations, this had to be avoided in the present experiment, which was affected by dissolving the required nutrient salts, with the exception of the sulfate, in distilled water. The sulfur required as physiological element had to be taken by the microbes from the chopped straw (cellulose) in the fermentation cultures. In the course of the experiment a little hydrogen sulfide could be observed, but it could only have originated from microbe albumen, as there was no sulfate present.

As it appeared that cellulose-methane fermentation cultures readily absorb hydrogen gas, this fact, just as with sulfate reduction, indicates that the combined oxygen of the carbonic acid as hydrogen acceptor, must be regarded as the depolarizer of the above iron corrosion process.

Cellulose-methane fermentation is very general in marshy and boggy districts, so this is a common process in the ground in the low-lying polder country in the Netherlands.

Söhngen's observation that cellulose-methane fermentation and sulfate reduction may take place simultaneously, is proved conclusively from the local examination of the soil in the above districts, so that in these cases the iron is exposed to the aggressiveness of the two processes at the same time.

On the destruction of the cellulose due to the methane fermentation, several soluble organic compounds are formed, which is of importance for the sulfate reducing spirilla, as these microbes can only absorb dissolved organic food.

The frequent occurrence of these two anaerobic processes simultaneously implies the possibility that, in cases of anaerobic iron corrosion in marshy and boggy soils, not only sulfate reduction but also cellulose-methane fermentation takes an active part. This will also be the case with the corrosion of iron sinkers in canals where an intensive sulfate reduction and cellulose-methane fermentation prevail at some depth and especially in the mud, owing to the continuous influx of sewage. Corrosion of iron pipes may also take place, when pipes in the neighborhood of manure heaps and rubbish dumps, are buried under the material of these organic waste products, as, according to Déhérain[18], a powerful methane fermentation can develop in manure heaps.

As far as the experiments are concerned with samples of soil corrosive to iron, which were placed in sealed bottles with a manometric apparatus attached, it was always found that the iron put in was attached with formation of iron sulfide without an increasing rise in pressure being observed. This would have been the case if methane had been formed by the carbonic acid reduction process, as, according to Söhngen[19] methane is not assimilated by sulfate reducing microbes. This would indicate that in nature the sulfate reduction

maintains its supremacy in these soils under anaerobic conditions.

The iron corrosion process under consideration, takes place, just as in the case of the corrosion of iron by sulfate reduction, only if the condition (c) (given at the beginning of this chapter) is complied with. This *is* the case as the oxygen from the carbonic acid acts as hydrogen acceptor.

From the electrochemical point of view, anaerobic corrosion of iron by the carbonic acid reduction process can be considered in a manner analogous to that of iron corrosion by sulfate reduction. In the present corrosion process which takes place according to the reaction diagram:

$$4\,Fe + 6\,H_2O + CO_2 \rightarrow$$
$$4\,Fe(OH)_2 + CH_4 \quad (10)$$
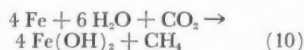
the value of $p_{Fe^{..}}$ in (4) is kept low, on the iron being anodically dissolved by the low solubility product of $Fe(OH)_2$ which is the only corrosion product. For the values of C_{H2} and $C_{H.}$ in (4) exactly the same applies as was observed with regard to sulfate reduction.

Iron Corrosion by Nitrate Reduction Process

In this microbiological process the hydrogen in the organic food is oxidized by the oxygen present in the form of nitrates. For this biological oxidation, applied to the hydrogen in the corrosion element, the equation:

$$HNO_3 + 8H \rightarrow NH_3 + 3\,H_2O \quad (11)$$

is applicable, which exothermic reaction supplies the nitrate reducing bacteria with the energy required for their vital functions.

This representation of the nitrate reduction process does not vary essentially from that given by H. A. Barker,[20] follows the views of Kluyver and Donker given in the consideration of the sulfate reduction process.

In connection with the anaerobic corrosion of iron the same fact applies to this process as in the case of sulfate and carbonic acid reduction, that the combined oxygen from the nitrate as hydrogen acceptor, has a depolarizing effect on the corrosion element.

In sulfate reduction the oxygen from the sulfate and in carbonic acid reduction the oxygen from the carbonic acid cannot, of themselves, oxidize the polarizing hydrogen, but this *is* the case with the oxygen present in the form of nitrates, as was already referred to in a general sense in Chapter 2.

On the other hand the oxygen present in the form of nitrates cannot of itself oxidize gaseous hydrogen, which power the nitrate reduction process *does* possess, as shown by Niklewski and Bronislaw[21] as early as 1914, which points to an activation of the oxygen present in the form of nitrates.

The depolarization in the case of iron corrosion by nitrate reduction may, therefore, be more intensive than the oxygen present in the form of nitrates is capable of producing of itself.

As far as is known, no case of definitely

recognized iron corrosion by the nitrate reduction process has ever been observed, so that this form of iron corrosion is only mentioned for the sake of completeness; more as a possibility than as an actual fact. Just as the corrosion of iron pipe lines may take place due to the methane fermentation of waste products in manure heaps, the possibility exists under the same conditions of iron corrosion due to the nitrate reduction process which may occur inside the manure heap.

In regard to the electrochemism of the case of corrosion under consideration, the same main points apply as mentioned in respect of iron corrosion due to the carbonic acid reduction process. The corrosion product in this case is also $Fe(OH)_2$. Nothing can be said with regard to the C_H. value as the investigations concerning this point are still proceeding.

As regards the manner in which the cathodic hydrogen is transferred in the case of anaerobic corrosion to the oxygen of the sulfate, carbonic acid and nitrate by the three microbiological processes mentioned above, which amounts to the depolarization of the cathode of the corrosion element, B. Elema's[22] investigations must be referred to. He investigated nitrate reduction in connection with the occurrence of an oxido-reduction potential in this process, in which he indicated a reversible oxido-reduction system called bio-indicator, formed in the metabolic process, as the transmitting medium. From the point of view of the analogy of nitrate reduction to sulfate and carbonic acid reduction this assumption is also applicable to these two processes. Each of the three kinds of anaerobic iron corrosion dealt with may be considered as an electro-chemical corrosion in which the bio-chemical reduction process as hydrogen acceptor acts as depolarizer in the corrosion element and may, therefore, be called an electro-bio-chemical process.

Finally it may be remarked with regard to anaerobic iron corrosion that the preceding facts show that the parts of the mechanism are by no means new. This *is,* however, the case with the bond that unites the whole, and which gives a new insight into the anaerobic iron corrosion process.

Iron Corrosion Due To Chemical Substances In The Soil

As early as 1863 J. M. van Bemmelen mentioned in his work published in "Scheikundige verhandelingen en onderzoekingen"[23] a process in the soil by which hydrogen sulfide and iron sulfide are formed by the rotting of vegetable remains in the presence of gypsum. The above observations were confirmed by the results of the investigation of the soils in the polders of the former Y, reclaimed in 1870-1878 made likewise by Van Bemmelen.[24] There is no doubt that this amounts to nothing else than the sulfate reduction process which has already been discussed at length above.

In Van Bemmelen's[25] second treatise the occurrence of pyrites and free sulfur in the ground formed by the rotting process described by him and now known as sulfate reduction of which many

particulars are given, is, however, very remarkable.

On consideration it is obvious from a chemical point of view in what way pyrites and free sulfur were formed in sulfate reduction in the polder soil, in which all the conditions of this process are usually complied with.

The hydrogen sulfide released is oxidized by the hydrated ferric oxide generally present in the soil according to the equation:

$$3\,H_2S + 2Fe(OH)_3 \rightarrow 2\,FeS + S + 6H_2O \quad (12)$$
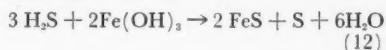
while pyrites are formed by the action of sulfur on iron sulfide:

$$FeS + S \rightarrow FeS_2.$$
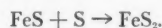
When sulfate reduction is prevailing in the soil, the presence of sulfur may, therefore, be regarded as an intermediate stage, preceding the formation of pyrites.

In the laboratory the formation of pyrites in sulfate reduction cultures can be demonstrated by adding $Fe(OH)_3$ and after some time testing the sediment in the culture liquid for FeS_2. To this end the deposit is heated with diluted sulfuric acid in a flask till a damp lead acetate paper no longer darkens, which proves that all the iron sulfide (FeS) present has been decomposed. (FeS, is not attacked by dilute acids). If small pieces of pure zinc are then added to the still acid solution a damp lead acetate paper will again darken, if FeS_2 is present, due to hydrogen sulfide formed from the reduction of the pyrites.

This simple method of indicating pyrites, generally a non-readily soluble polysulfide, is not novel but it is described here once more, as it seems to be little known.

Therefore, it appears from the experiment described, that Van Bemmelen's view regarding the formation of pyrites (and sulfur) in the rotting process in the ground in the presence of gypsum (sulfate reduction) and ferric-oxide as referred to by him, is quite correct.

The importance of the possibility of pyrites and free sulfur occuring in soils in which sulfate reduction is taking place or has taken place, lies in the fact that both substances are aggressive to iron. It has already been stated before that free sulfur is a powerful hydrogen acceptor in anaerobic iron corrosion, while in the case of pyrites the combined polysulfide sulfur acts as such.

With the corrosion of iron pipes in soils with sulfate reduction two cases may be distinguished. In the first case the iron is attacked not only by active sulfate reduction but also by pyrites and sulfur if these are formed. In the second case the iron pipe lines will only be corroded by pyrites and sulfur which may be present, if the sulfate reduction has ceased owing to the lack of the necessary sulfate or other food.

In soils with sulfate reduction varying quantities as well as traces of pyrites and sulfur were found to be present. This possibly depends on the intensity of this anaerobic process as well as on the presence of readily or non-readily re-

ducible ferrous compounds. Contrary to the indication of pyrites in the above soils by means of the reduction method described, which was very simple, the test for the presence of free sulfur was not. Finally sulfur was separated by means of an extracting agent in the form of the readily recognizable light yellow crystals.

It might be thought that, with iron corrosion by the sulfate reduction process, the dark layer of crust of corrosion products on the deteriorated surface of the iron can contain neither pyrites nor sulfur as these substances immediately disappear in the fulfillment of their role of hydrogen acceptor. The investigation of the corrosion products so formed has, however, shown that both pyrites and sulfur may be present in larger or smaller quantities. This leads to the conclusion that during the corrosion of the iron both these substances may appear and disappear, increasing the aggressiveness of the corrosion process by their cooperation.

It was already pointed out above that the hydrated ferric oxide in the soil may affect the oxidation of the hydrogen sulfide originating from sulfate reduction. It need, therefore, cause no astonishment that it is also capable of oxidizing the cathodic hydrogen from the corrosion element, so that this substance may also act as a hydrogen acceptor in anaerobic iron corrosion. As this property of hydrated ferric oxide is more evident in the aerobic corrosion process a further explanation will be given of this in due course.

The three substances discussed, pyrites, free sulfur and hydrated ferric oxide (if they are present in the soil) form the hydrogen acceptors required under point (c) of this chapter to affect the corrosion of iron in an anaerobic manner.

The electrochemical condition expressed in (4) is fulfilled in the cases of corrosion considered in the same manner as indicated with respect to the sulfate and carbonic acid reduction, as they are of a neutral character as was the case with the processes just mentioned.

CHAPTER 4
The Aerobic Iron Corrosion Process

The extensive literature already existing on the subject of the aerobic corrosion of iron, renders it superfluous to repeat in this treatise the facts already known about this process. It is therefore intended to discuss the aerobic corrosion process in the ground only in so far as it is characterized as a result of the aeration of soils with sulfate reduction. This has already been referred to at the beginning of Chapter 3.

Apart from a side effect, which will be referred to in due course, mainly the oxygen from the air as hydrogen acceptator acts as the depolarizer in the corrosion element in the aerobic iron corrosion process. Although a mixture of corrosion products is usually formed in this corrosion process which are partly in the ferric, partly in the ferrous condition, the former predominate to such an extent that the ferric condition of

the above substances may be considered as a feature of aerobic corrosion.

Soils which have become iron sulfide-containing owing to sulfate reduction, will show an acid reaction when they are aerated owing to the drying of the soil or a fall in the level of the ground water. This could be observed with samples of soil kept in glass pots and at first showing sulfate reduction. They then showed a neutral or slightly alkaline reaction, but when air was admitted they showed a strongly acid reaction after several weeks.

According to Van Bemmelen, P. J. Van Kerckhoff was the first research worker to point out that these acid soils contain ferrous sulfate which, according to him, was probably formed by the oxidation of iron sulfide. In a further investigation Van Bemmelen[26] ascribed the formation of acid in the soil to the oxidation of the pyrites, in which case, he asserts, ferric sulfate and sulfuric acid are formed. This is to be understood to mean that, on hydrolysis, the ferric sulfate changes into yellow basic ferric-sulfate, which is often encountered in the low-lying polder districts in the Netherlands, with a simultaneous separation of sulfuric acid. D. J. Hissink[27] states that the formation of acid due to oxidation of accumulated sulfides can produce higher degrees of acidity if there are no basic elements present in the ground. It need hardly be said that iron pipes are intensively attacked in such acid soils.

The very prevalent opinion that the corrosion of iron in the air by ferric sulfate is the result of the ordinary action of acid is quite incorrect. In order to obtain a correct conception of the chemism of this corrosion process, iron was exposed both with admission and with exclusion of air to the action of a diluted ferric-sulfate solution, it being impossible in this experiment to use ferric-sulfate formed in a natural manner. As this ferric sulfate solution also yields sulfuric acid as a result of hydrolysis, the outcome of this test therefore applies equally to the iron corrosion process by ferric-sulfate formed in a natural manner, as far as the principle of the chemism of iron corrosion is concerned.

Only in the beginning did the anaerobic iron corrosion in a ferric-sulfate solution of 0.25 percent concentration take place under development of free hydrogen, it gradually diminished and finally as good as ceased altogether while the p_H of the solution rose from 1.5 to 6.0.

Also with the aerobic corrosion test free hydrogen only developed in the beginning, the corrosion consequently being more intensive in the beginning, but in contrast with the anaerobic test the corrosion of the iron continues practically constantly, whilst the p_H after having risen from 1.5 to about 4.0 does not alter appreciably. It is clear that the characteristic feature of the latter test lies in the fact that there is only a constant continuation of iron corrosion when air has access and the degree of acidity of the medium is practically constant.

There can be no other theoretical interpretation than the following. The corrosion of the iron, after the normal corrosion due to the acid, which necessarily involves a rise in pH, has ceased, will be able to proceed continuously, owing to the oxygen from the air as hydrogen acceptor causing depolarization in the corrosion element. This may also occur in an indirect manner owing to the ferric compounds acting as hydrogen acceptors and passing into the ferrous condition. By oxidation in the air it returns to the original ferric form, so that the hydrogen acceptor is again recovered. There is therefore a regeneration of the hydrogen acceptor in this case. The pH of the acid solution finally adjusts itself to a constant value while the deteriorated iron passes into a ferric-oxide which is insoluble in this.

It follows from a consideration of equation (4) that, if there are no disturbing influences present, this aerobic iron corrosion process takes place with a constant degree of acidity and is stimulated by the low pH prevailing, as the electromotive force of the corrosion element $E_H - E_{Fe}$ rises much more than would be the case if it worked in a neutral medium. (As E_{Fe} is also negative according to (3) E_H will be much less negative with respect to this value, in consequence of the higher concentration of hydrogen-ions C_H in equation (4), so that $E_H - E_{Fe}$ is a large positive number.) As in all other cases of corrosion the C_{H2}-value is also kept low in this case by depolarization.

In connection with the aerobic iron corrosion process in acid soils, the use of lime or chalk is generally recommended in order to neutralize the acid present and so protect the iron pipes from being attacked. As can be seen above, this precaution is only effective with regard to the influence of the degree of acidity in the corrosion process. After the neutralization of the acid ferric-compounds are still present, which as such are hydrogen acceptors and may affect the corrosion of the iron. This fact was also experienced by W. Palmaer.[28] Wet rust on metallic iron also causes further rusting for the same reason, so that in the ordinary process of rusting not only oxygen from the air, but also the rest formed $(Fe(OH)_3)$ acts as hydrogen acceptor in the depolarization in the corrosion element. This side effect was already referred to at the beginning of this chapter. To this must be ascribed the fact that ordinary iron rust usually contains ferrous compounds besides the ferric compounds.

Another result of the aeration of soils containing iron sulfide due to sulfate reduction is the formation of pyrites to which Van Bemmelen[29] drew attention. In the case of soils which have become acid, due to the entrance of air, hydrogen sulfide may be released from the iron sulfide still present, yielding free sulfur on oxidation, which may in the same way be formed from hydrogen sulfide originating direct from sulfate reduction. The presence of ferric sulfate, pyrites and free sulfur, all aggressive to

iron, in soils which have become acid due to aeration, is the result of a preceding sulfate reduction so that these substances must be considered as the sequel to the sulfate reduction process.

If anaerobiosis again shows itself in the above acid soils due to a rise in the level of the ground water and closing off of the soil, the degree of acidity will gradually diminish owing to the absence of oxygen as hydrogen acceptor on account of the solution process of the iron till a pH value is again attained favorable to a renewed sulfate reduction process. In such soils aerobic and anaerobic iron corrosion may alternate in the manner described which is very injurious to iron pipe lines.

CHAPTER 5

The Hydrogen Acceptor Constitutes The Unity In The Anaerobic And Aerobic Iron Corrosion Processes In The Soil

After the explanation of the various ways in which iron corrosion in the soil is liable to occur, it has now become possible to consider the various forms of corrosion and their mutual relationship in more detail. Judging from the difference both in the appearance and the composition of the corrosion products, one would think at first sight that the cause of the corrosion was different too in every case. This view must be considered as untenable on the grounds of the electro-chemical views on metal corrosion, as this corrosion can always be traced back to the metal passing anodically into solution. For this reason the differences observed between individual cases of corrosion have to be accounted for by the conditions under which the corrosion process takes place. This is as a matter of fact always possible.

As was more fully explained in Chapter 3, it is a remarkable fact that in anaerobic condition corrosion does not always occur when a piece of iron is in metallic contact with the damp soil. This necessarily leads to the conclusion that another decisive factor must participate, if the potential property of the iron to act electro-chemically as a hydrogen donator becomes actual, or in other words if the corrosion process begins. It is obvious that this must be looked for in the depolarizer of the corrosion element, whilst the preceding chapters have shown that several substances can serve this purpose as hydrogen acceptors.

The hydrogen acceptor which is invariably present with all the forms of iron corrosion considered, both anaerobic, and aerobic, constitutes the unity of the iron corrosion process in general. This creates the possibility that the various forms of iron corrosion, which, as has been seen, do not in reality differ, may in future be considered from one point of view, which means a considerable simplification of the views about the nature of the iron corrosion process in the soil.

Summary

Former investigations into the corrosion of iron pipe lines in soils were, up to 1922, only carried out with respect to the ordinary or *aerobic* corrosion (with oxygen from the air), whilst since that time in the Netherlands a commencement has been made with the study of *anaerobic* iron corrosion in the soil (without oxygen from the air). This important process has also been investigated in various other countries since 1922.

The investigations made in the Netherlands since 1922 into the process of anaerobic corrosion showed that this was principally of a micro-biological nature.

The primary corrosion process in which iron acts as a hydrogen donator:

$$Fe + 2H^{\cdot} \rightarrow Fe^{\cdot\cdot} + 2H$$
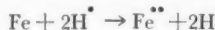
only proceeds uninterruptedly when a hydrogen acceptor acting as depolarizer in the corrosion element is present. The following proved to be able to act as such.

1. The *sulfate reduction* of Beijerinck, according to Baars' scheme and following Kluyver and Donker:

$$H_2SO_4 + 8H \rightarrow H_2S + 4H_2O$$

The reaction of the iron corrosion is:
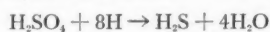
$$4Fe + H_2SO_4 + 2H_2O \rightarrow$$
$$3Fe(OH)_2 + FeS$$
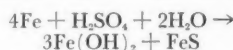
The remarkable thing about this anaerobic iron corrosion process which is often very serious and which is often encountered in the low-lying polder districts of the Netherlands, lying in many cases below sea level, is the fact that it often takes place in practically neutral surroundings (pH = about 7). This is accounted for by the formation of the corrosion products $Fe(OH)_2$ and FeS as shown in the above equation. These are neutral in character. In this connection there is no question of corrosion of the iron by hydrogen sulfide as no free hydrogen is developed and as the proportion $\dfrac{Fe}{FeS}$ mentioned in Chapter 3 under sulfate reduction would have to be equal to 1.

But theoretically the value 4 would follow from the above equation of iron corrosion. The values 2.4 to 3.4 found experimentally correspond satisfactorily to this value in the circumstances mentioned in Chapter 3.

2. The carbonic acid reduction of Söhngen (1906):

$$CO_2 + 8H \rightarrow CH_4 + 2H_2O$$

The reaction of the iron corrosion is:

$$4Fe + 6H_2O + CO_2 \rightarrow 4Fe(OH)_2 + CH_4$$
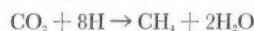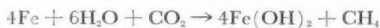
As the iron so corroded passes into Fe (OH)₂ the reaction of the medium also remains practically neutral (pH = about 7).

As carbonic acid reduction occurs in cellulose-methane fermentations and these are generally prevalent in the marshes and bogs of the polder districts of the Netherlands, these soil conditions comply with the requirements of this iron corrosion process. These conditions are also complied with in the mud of canals into which the town sewage is discharged. This is detrimental to the iron sinkers which are present in them.

Manure heaps and rubbish sumps with organic refuse of varied origin which may also give rise to a powerful methane fermentation, also constitute a possibility of the corrosion of iron pipes if they get buried under these substances.

Usually methane fermentation and sulfate reduction occur simultaneously, so that both processes have a deteriorating action on iron.

As far as the corrosion processes in the soil are concerned it would seem that the sulfate reduction predominates.

3. The nitrate reduction, with biological oxidation, applied to the hydrogen of the corrosion element, devolves to the equation given by Barker, after Kluyver and Donker:

$$HNO_3 + 8H \rightarrow NH_3 + 3H_2O$$
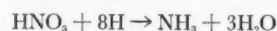
As anaerobic iron corrosion due to the nitrate reduction process has not yet been ascertained in practice and the investigation into this form of corrosion is still incomplete, it is mentioned rather as a possibility than as an actual fact. The milieu of organic refuse containing nitrogen, such as manure heaps, present the conditions which render this form of iron corrosion possible

These three microbiological processes concerned in the anaerobic iron corrosion affect the depolarization in the corrosion element in the electro-chemical deterioration of the iron, so that they may be referred to as *electro-biochemical* processes.

4. Chemical substances.

As early as 1886 Van Bemmelen proved the presence in soils of pyrites and free sulfur formed by sulfate reduction in the presence of ferric hydroxide. These substances are also capable of deteriorating iron anaerobically.

The acid soils which are very aggressive to iron and which were first studied by Van Kerckhoff, have been formed by the aeration—as a result of the drying of the soil or a fall in the level of the ground water—of iron sulfide, originating from sulfate reduction, present therein.

According to Van Bemmelen (1886) ferric sulfate and sulfuric acid are formed when air enters the soil, especially owing to oxidation of iron sulfide in the form of pyrites. The interpretation of this phenomenon must, therefore, be that ferric sulfate, on hydrolysis accompanied by a separation of sulfuric acid, passes into basic ferric sulfate which is often encountered in the low-lying polders of the Netherlands as a yellow compound.

The corrosion of iron in aerated acid soils is found to take place with a constant degree of acidity, as long as no disturbing influences are present. The low pH of the medium considerably promotes the process. Hence the seriousness of this form of corrosion. The general opinion that this is a case of ordinary deterioration of the iron due to the acid coupled with the development of free hydrogen, must, therefore, be considered as wrong. On the addition of lime or chalk to the soils with a view to preventing iron corrosion, it must be remembered that by doing this only the neutralization of the

acid is affected, but the ferric compounds present remain aggressive to iron, so that the remedy applied is not quite effectual.

Van Bemmelen asserted that the areation of soils containing iron sulfide originating from sulfate reduction also causes the formation of pyrites. Further free hydrogen sulfide, whether it is formed by sulfate reduction or by the action of acid on any iron sulfide that may still be present in acid soils, yields free sulfur on oxidation in the air. Such substances as ferric sulfate, pyrites and free sulfur, formed in the soil on aeration from products resulting from sulfate reduction, all of which are aggressive to iron, must, therefore, be considered as a sequel to the sulfate reduction process.

If acidic soils become anaerobic again, the degree of acidity gradually diminishes until a pH is attained which favors a renewal of the sulfate reduction. This alternation of aerobiosis and anaerobiosis in the above soils has proved to be very injurious to iron pipe lines.

The potential property of solid iron to act electro-chemically in the damp soil as a hydrogen donator is converted into an actual one by the hydrogen acceptor present in every form of iron corrosion.

The hydrogen acceptor, therefore, constitutes the *unity* on which all iron corrosion processes, regardless of any possible differences, are based.

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Devices Used in Corrosion Control of Power Cables*

By J. J. POKORNY

Introduction

CONTROL OF the corrosion of underground power cables depends to a considerable extent on the use of special electrical devices. The devices as described here are not new, but improvements have been made which have resulted in improved operation.

It is not the purpose of this paper to discuss the entire field of mitigation of the corrosion of power cables. The theory and practice of this phase of corrosion protection has been thoroughly developed over a long period of time. The paper is limited to a description of the improved equipment, and the part which each device plays in the control of corrosion.

In Cleveland the bulk of cable sheath corrosion is still due largely to stray currents. While the street railway cars have been discontinued for several years, trolley coaches are in operation and the negative trolley of this system is connected to the buried rail system which has remained in the streets. There is also an electric rapid transit system on railroad right-of-way which contributes to the stray currents because the converter and rectifier stations supplying these two systems are interconnected.

Reverse Current Switch

One of the primary problems in the control of stray current corrosion is the necessity for returning stray current to the originating station. This is accomplished by bonding connections to the negative system or to some other structure which can then carry the return current to the negative system. However, a reverse current switch is needed to disconnect the circuit when reversals occur due to load changes and to changes in station operation.

Many types of reverse current switches have been designed and used throughout the era of street railway operation and it may seem superfluous to describe still another one. However, the switch described here incorporates some novel features and may, therefore, be of interest.

The switch is shown in Figure 1 and the schematic diagram is shown in Figure 2. The entire equipment is mounted in a standard weatherproof meter box. One of the novel features of the switch is the separation of the heavy current carrying parts of the switch, namely the contactor and the protective fuse, from the control portion of the circuit. The control unit is shown in Figure 1 in the upper portion of the switch box. It is shock mounted to prevent vibration when the contactor operates. Figures 3 and 4 show two views

of the control unit, removed from the switch. Figure 3 is the top view and Figure 4 is the bottom view of the control unit chassis.

The functioning of the switch depends on an Edison Model 219 polarized relay. This relay operates in the plus and minus directions on a voltage of 5 millivolts and can take up to 0.5 volt across the coils when the coils are in series connection.

The operation of the switch is best explained by reference to the diagram in Figure 2. Polarity sensing pilot wires are connected from the cable and rail to the coils of the polarized relay RY1. Ahead of the polarized relay, however, there is interposed a relay RY2 which is calibrated to operate at 0.5 volt. This relay opens its normally closed contacts when the open circuit voltage between the cable and rail reaches 0.5 volt. This introduces a 40-ohm resistor to protect the polarized relay. In addition to the protective relay, RY2, there is also a filter circuit ahead of the polarized relay consisting of a 1.0 microfarad shunt capacitor and the 6.3 volt secondary of a filament transformer. This filter circuit protects the polarized relay against very steep transient current pulses which were found to be demagnetizing the relay and sometimes reversing its polarity.

Assuming the switch to be in an open position, upon receiving at 5 millivolt or greater positive impulse, the polarized

Abstract

This paper describes the various devices which are used in the corrosion control of underground power cables. Many of these devices have been used for a long time but the present paper describes a number of useful improvements in such devices as the electrolysis switch, the test current interrupter, and the cathodic protection and forced drainage rectifiers. The use of silicon power rectifier as an electrolysis switch is described. A method of grounding and corrosion protection of a pipe cable system is also outlined.   7.7, 5.2.1
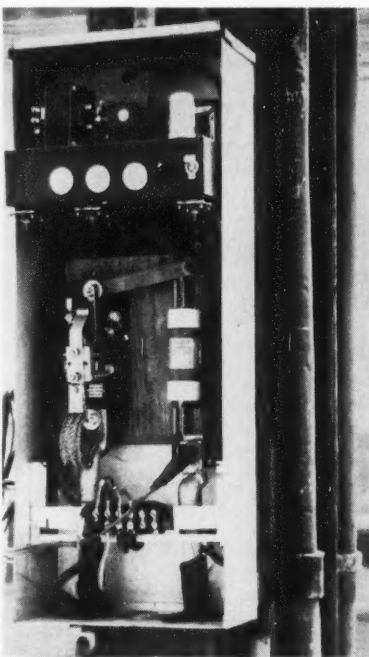
Figure 1—Reverse current switch.
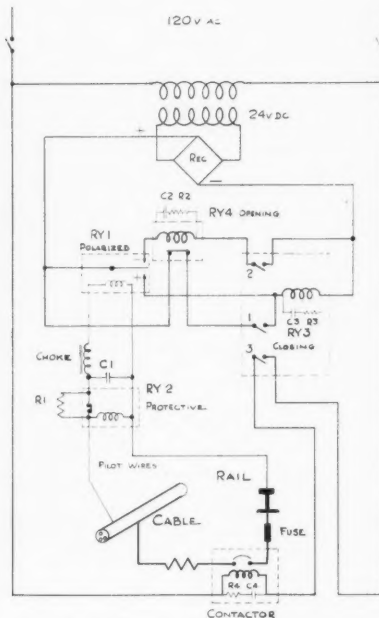
Figure 2—Diagram of reverse current switch.
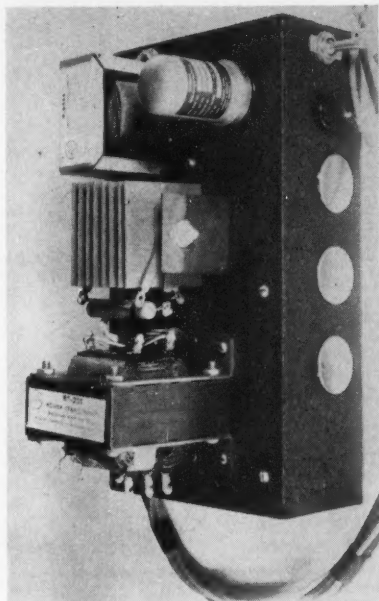
Figure 3—Control unit for reverse current switch.

Figure 5—Forced drainage rectifier.

Figure 6—Small cathodic protection rectifier.

Figure 4—Chassis for control unit.

relay closes and energizes the closing relay RY3. The number 1 contacts on the RY3 relay short circuit the positive contact on the polarized relay and thus lock-in the closing relay. The closing relay, therefore, does not depend on the polarized relay to remain closed, but remains closed until a negative impulse is received. The number 3 contacts of the closing relay close the main contactor. The number 2 contacts are in series with the coil of the opening relay RY4 and by being open except when the RY3 relay is closed they prevent unnecessary impulses through the opening relay and unnecessary burning of the negative contacts of the polarized relay. Once the switch opens no further action takes place until after the switch closes, no matter how many times the negative contact is made.

The normally closed contacts of the opening relay RY4 are in series with the lock-in contacts of the closing relay RY3. Therefore, when a negative impulse is received and the opening relay, RY4 opens, relay RY3 opens and the contactor also opens.

The relay contacts are protected against burning due to inductive load by means of the resistors and capacitors which are across the relay coils. The main drainage circuit is protected against faults on the trolley system and unexpectedly high drainage currents by means of a fuse. The amount of drainage is controlled by means of a series grid resistor in the drainage circuit. This grid resistor also provides the necessary 5 millivolt drop for opening the switch when a current reversal occurs.

Rectifiers and Cathodic Protection
Forced Drainage

In situations where it is desirable to drain a cable system, but the voltage conditions between the cable and rail are such that drainage cannot be accomplished by means of a simple drainage connection, a rectifier can be used to force the drainage to go from the cable to the rail.

The rectifiers used for this purpose are essentially the same as the rectifier used for cathodic protection. Frequently it is possible to design a rectifier for a specifc situation. In such cases the design can be held to the minimum essential components. Such a rectifier is shown in Figure 5. This rectifier incorporates no meters or voltage regulator. Adequate voltage selection, however, can be obtained by means of a number of transformer taps.

When this rectifier was placed in operation it was found that the current variations were quite violent varying from zero to 15 amperes. The drainage current was stabilized by the insertion of a 150 watt ballast lamp in series with the primary of the rectifier transformer. This reduced the current variations to a range of from 8 to 10 amperes. It also reduced the voltage to ground fluctuations.
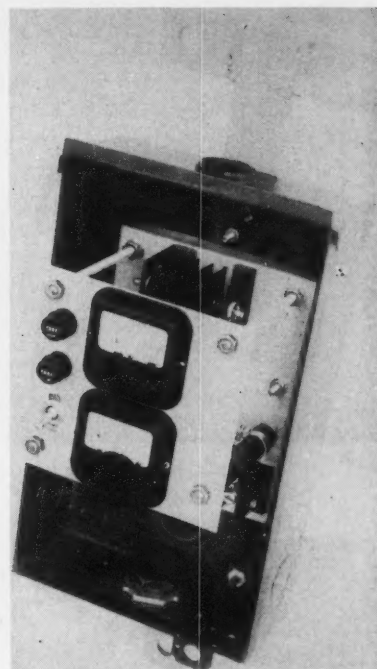
Cathodic Protection

The second use of rectifiers, of course, is for cathodic protection including in most cases protection against stray currents. This type of rectifier is used largely on isolated cable sections, which may be isolated either because they are connected to overhead circuits or because they have been deliberately isolated by means of insulating joints.

Cathodic protection rectifiers are also used to protect the steel pipes in pipe-type cable systems. In all cases they are used in connection with standard buried ground beds. Some of these ground beds consist of standard graphite rods buried in the floor of a nearby manhole, or when it is convenient, the ground beds are installed in substation yards.

The types and sizes of cathodic protection rectifiers vary over a wide range. One of the smallest rectifiers has recently been placed in operation to protect an isolated section of cable, 1900 feet long. This rectifier is shown in Figure 6. The rectifier is assembled in a standard meter box. It has a capacity of 5 volts and 1 ampere d-c and is actually operating at 1.8 volts and 0.4 amperes. In this case it is protecting a section of cable on private property, which is isolated from the rest of the underground system.
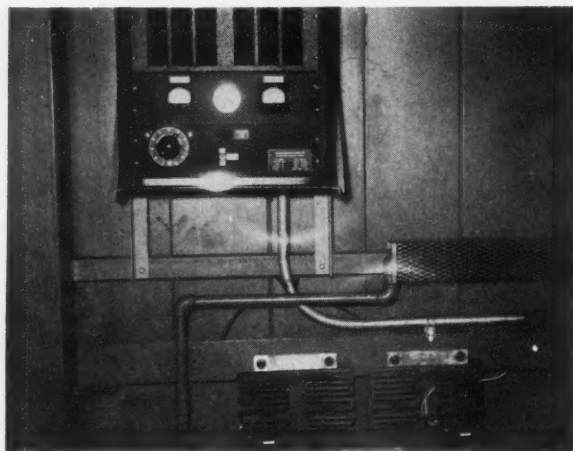
Figure 7—Cathodic protection for pipe type cable.

Figure 8—Diagram of cathodic protection for pipe type cable.

Figure 9—Arc gap for pipe type cable protection.
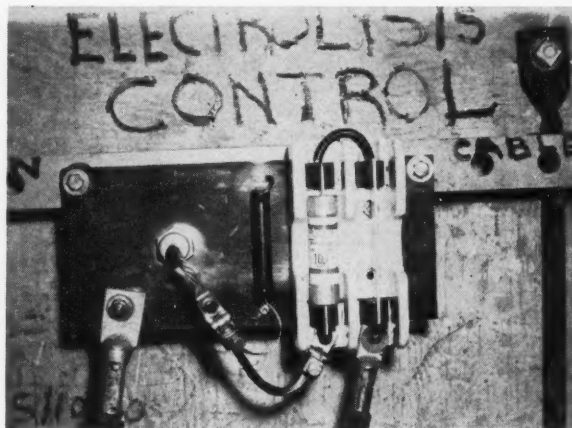
Figure 10—Silicone diode used as reverse current switch.

Pipe-Type Cable Protection

Cathodic protection of pipe-type cables has received much attention in recent years. The problem is similar to the problems of protecting any other type of pipe line. There is, however, some additional complexity due to the necessity of providing a path for the return of fault currents during ground faults. These ground fault currents flow along the steel pipe and must return to the station or transformer neutral.

In some installations it has been customary to use the station ground as an anode bed, connecting the protective rectifier between the pipe line and the station ground. This type of installation, however, exposes the station ground to a positive polarity which could result in electrolytic damage to the station ground at some obscure point, in case of uneven current distribution.

The protective system described in this paper was, therefore, designed with a separate graphite anode bed. In this system the station ground is connected to the negative pole of the rectifier through a set of grid resistors. This arrangement is shown in the photograph in Figure 7 and in the diagram in Figure

8. The rectifier has a capacity of 30 volts and 24 amperes. The resistors first provide the needed metallic path for fault currents which must flow from the pipe to the station ground. They also hold the rectifier current which flows between the station ground and the graphite ground to a reasonably low value. In this case the rectifier current divides approximately in the proportion of 2 amperes protective current to the pipe and 10 amperes through the resistors to the station ground. There is some superposition of variable stray current on the system. A benefit which is derived in this installation is that the station ground obtains some cathodic protection instead of being subject to possible damage.

The size of the resistors depends on several factors. While it must be high enough to hold the rectifier current down, it must not be so high as to permit excessive voltage to develop during fault conditions. The resistor in the present installation has a value of 0.1 ohm. The resistor must also have enough current carrying capacity to carry the fault
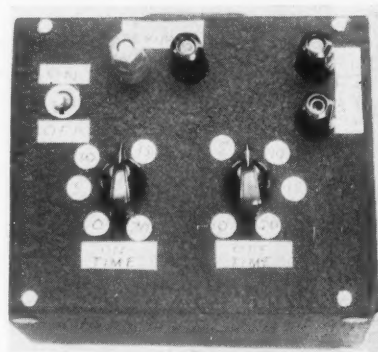
Figure 11—Interrupter switch.

current. The current carrying capacity was determined by a method described by Kulman.[1]

During a ground fault the voltage across the resistor grids can rise several hundred volts. While the resistors are capable of withstanding this voltage and carrying the resulting current, fur-
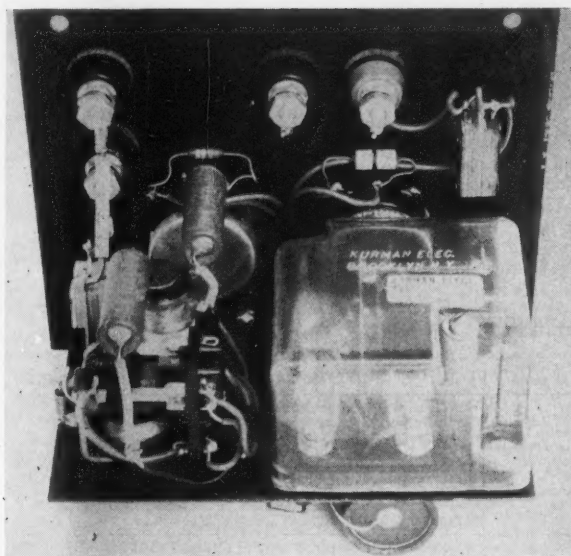
Figure 12—Chassis of interrupter switch.
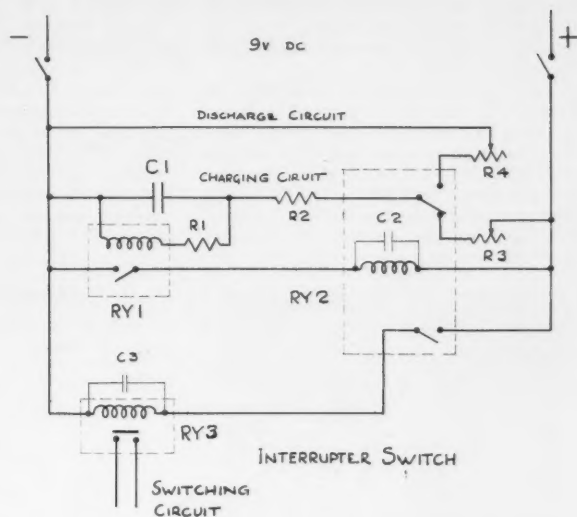
Figure 13—Diagram of interrupter switch.

ther protection has been provided in the spark gaps which are connected between the pipe and the station ground. One of the gaps is shown in Figure 9.

The gaps consist of two $\frac{1}{4}$ x 4 x 8 inch busbar plates held together by two pressure plates. The actual gap area is 4 x 4 inches. The pressure plates are insulated from the gap plates by means of a $\frac{1}{8}$ inch thick fibreglass-melamine insulating plate. The plates which form the gap are separated by four strips of polyvinylchloride tape, and the assembly is taped to keep out moisture. It is desirable to have these gaps arc over at as low a voltage as possible, but without arcing during ordinary switching transients or remote lighting on overhead lines. The 7-mil tape has permitted the gaps to arc unnecessarily and, therefore, further investigation is necessary to find the optimum gap thickness. Figure 9 shows the method of mounting and connecting the gaps. One of the gap plates is bolted to the grounded steel structure and the other is connected to the copper riser pipe by means of a standard tubular bus connector and a piece of 500,000 cm rubber insulated cable.

Silicon Diode

A somewhat different use of a rectifier has come into use recently, namely, as a substitute for the reverse current switch. This application of rectifiers has been used in the past but the introduction of the high current silicon diode has made this application much more feasible. Previous forms of rectifiers have been bulky when large currents had to be drained unidirectionally.

The high current diode, however, is an extremely compact device, and even with its associated heat sink occupies very little space.

An installation of a silicon diode used as a reverse current switch is shown in

Figure 10. The diode assembly in this installation is located at a rapid transit supply station where reversals of current occurred when the drainage connection consisted only of a simple metallic connection.

The diode is mounted on a large copper plate which has been blackened by an electrolytic process. The copper plate acts as a mounting plate as well as a heat sink. A 25-ohm resistor is connected across the diode to limit reverse voltage surges which, for this diode, should not exceed 100 volts. The diode is rated at 100 amperes in this assembly. In the present installation there is a tendency for the current to peak sharply. This tendency is being controlled temporarily by means of a bank of five street lighting lamps in parallel as ballast. Some permanent solution of this problem is being investigated.

The principal limitation in the use of the silicon diode as a reverse current switch is that it can only be used where sufficient voltage is available to cause the desired drainage current to flow in the forward direction. The diode will effectively stop the current flow in the reverse direction but very little current would drain unless the voltage were at least 0.5 volt, and normally about 1 volt is required. This is in contrast with the reverse current switch which operates on reversals of 5 millivolts.

Resistors

In addition to the use of resistors as already described in connection with the cathodic protection of pipe-type cable, extensive use is made of cast iron resistors for other purposes of stray current control. In most drainage connections it is desirable to maintain the drainage currents at a minimum. Drainage currents greater than necessary not only require unnecessarily large connections, but also increase the current pick-up, which sometimes results in cathodic

corrosion in the cathodic area. Grid resistors mounted on the manhole wall are effective in adjusting the drainage current to a desired amount.

Resistors are also useful in connection with insulating joints. When insulating joints are installed in sheaths of cables in an ungrounded system there is no fault current in the sheath during a cable fault. In a grounded neutral system, however, the current during a ground fault must have a path back to the station neutral; otherwise arcing to ground could occur at some points along the cable run. Insulating joints installed in a grounded neutral system should, therefore, be bridged by means of suitable resistors, unless some other path is provided for the fault current to return to the station neutral.

Jacketed Cable

While jacketed cable does not belong in the category of electrical devices its function is intimately associated with electrolysis control and it is, therefore, mentioned here in order to complete the record.

Jacketed cable may be used both in anodic and cathodic areas, to control corrosion. Where the cable sheath is anodic and there is no other convenient solution for the problem, jacketed cable will stop any further corrosion when all of the cable in the area is replaced. Sometimes it is more convenient to install jacketed cable in the cathodic area. This occurs when the area where current is picked up is small and the anodic area is extensive. In such cases insulating the cable in the cathodic area breaks the circuit of the corrosion current and thus stops the current flow and with it the corrosion in the anodic area.

Interrupter Switch

The interrupter switch is an auxiliary device which though not strictly used in the control of corrosion, is useful in

making tests. There are many designs of interrupter switches, some depending on mechanical switching, many others depending on the time constant of a capacitor-resistor circuit.

The interrupter switch illustrated in Figures 11 and 12 is a very simple device which does not require any electronic equipment, but only the c-r circuits and three relays. A schematic diagram is shown in Figure 13. The operation of the switch depends on charging the capacitor C-1 through the variable

resistor R-3 and discharging it through the resistor R-4. The capacitor is first charged through R-3 which determines the "off" time.

When the voltage across C-1 becomes high enough to operate relay RY1, which is adjusted to operate at 0.3 milliampere, this relay closes its contacts and operates relay RY2. The operation of relay RY2 operates the switching circuit and also transfers the capacitor C-1 from the charging resistor R-3 to the discharge resistor R-4. The relay RY1 opens when

the current drops to 0.15 milliamperes, The discharge time determines the "on" time for the interrupter switch.

Acknowledgments

The design and application of the devices described has been in most cases worked out by E. T. Schneider and G. E. Thomas, both of the Cleveland Electric Illuminating Company.

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APPENDIX PARTS LIST

Quantity	Description	Mark
	Reverse Current Switch Figures 1, 2, 3 and 4	
1	Relay, sensitive d-c (Polarized), SPDT, Thomas A. Edison Co. No. 219-A-3-AA (Coil Res.-0.5 ohm ea., setting-5.0 ma.)	RY1
1	Selenium Rectifier Transformer, 110 volt/24 volt @ 1.25 amp-Stancor No. RT-201	....
1	Selenium rectifier & brackets, 52 volt a-c at 1.4 amp d-c Radio Receptor No. S2B1S1GJ6	Rec.
1	Relay, 24 volt d-c Coil-Guardian No. 200-2	RY4
1	Relay, 24 volt d-c Coil-Guardian No. 200-5	RY3
1	Relay, SPDT, (Parallel Coils & Adj. for 0.5 volt Pull-In)-Sigma No. 5F-1000-S-SIL	RY2
1	Transformer, 110 volt/6.3 volt = 3 amp-Stancor No. P-6466	Choke
3	Capacitor, Paper, 1.0 MFD., 600 volt-Mallory No. GEM-61	C2, C3, C4
1	Capacitor, Paper, 1.0 MFD., 200 volt-Cornell Dubilier No. CUB-2WI	C1
2	Resistor, 1,000 ohm, 1 watt-IRC No. BW-1	R2, R3
1	Resistor, 1,500 ohm, 5 watts-Ohmite "Brown Devel"	R4
1	Resistor, 40 ohm, 10 watts-Ohmite "Brown Devel"	R1
1	Optional 250 amp, 115 volt a-c Coil	Contactor
	Forced Drainage Rectifier Figure 5	
1	Transformer, Stancor No. RT-208	....
	Taps from 12 to 29 volt, d-c output volt 9 to 24 volt	....
1	Selenium Rectifier Radio Receptor No. D-112	....
	Maximum d-c output 16 amps	....
	Maximum a-c input 25 volts	....
	D-C output 20 volts	....

Quantity	Description	Mark
	Cathodic Protection Rectifier Figure 6	
1	Transformer, Stancor No. P-6134 117/6.3 volt, 1.2 amp	....
1	Selenium Rectifier, Bridge Type, Radio Receptor No. D-109 1.5 amp capacity	....
1	Resistor, adjustable 25 ohm, 50 watt, Ohmite No. 0561	....
1	Voltmeter 0-6 volt d-c	....
1	Ammeter 0-1 amp d-c	....
	Cathodic Protection Rectifier Figure 7 and 8	
1	Powerstat Model No. 116U (0-140 volt, @ 7.5 amp)	TR-1
1	Rectifier Transformer Directron (2-18 volt @ 24 amp)	TR-2
1	Rectifier, Bridge Type, Selenium Radio-Receptor No. D-120 (24 amp d-c, 40 volt)	Rec.
1	Voltmeter Weston No. 1301, 0-30 volt d-c	V.
1	Ammeter Weston No. 1301, 0-30 amp d-c	A.
	Interrupter Switch Figures 11, 12, 13	
1	Relay, Kurman No. 310DC42 (Adjusted for 0.3 Ma. Pull in, 0.15 Ma. dropout)	RY1
1	Relay, Potter & Brumfield, No. KA11D (12 volt d-c coil) DPDT	RY2
1	Relay Potter & Brumfield No. MB3D (12 volt d-c coil) SPST-Double Break	RY3
1	Resistor, 4,700 ohms, ½ watt	R-1
1	Resistor, 10 ohms, 1 watt	R-2
1	Resistor, 10K W.W. Pot. IRC No. WPK (Off time charging)	R-3
1	Resistor 20K W.W. Pot. IRC WPK (On time, discharging)	R-4
1	Capacitor, 2,000 MF, 15 volt d-c (Electrolytic)	C-1
2	Capacitors, 4 MF, 50 volt d-c (Electrolytic)	C-2, C-3
1	Battery, 9 volt Burgess (4F6H)	....

Any discussion of this article not published above will appear in December, 1961 issue.

Corrosion of Superalloys at High Temperatures
In the Presence of Contaminating Salts*

By A. MOSKOWITZ and L. REDMERSKI

Introduction

IN CONTEMPLATING the use of a high-temperature alloy, corrosion resistance must be considered in addition to such mechanical properties as strength and creep resistance. Corrosive action seriously affecting service life may be produced in service by the presence of contaminants that are difficult to avoid. In particular, the presence of various contaminating salts could create serious corrosion problems for metals at high temperatures. Various studies have been made concerning the hot-salt corrosion of titanium and titanium alloys.[1-3] Because the salt appears to function as a catalyst in the corrosion of these alloys, trace quantities such as may be deposited by finger prints can lead to catastrophic attack. Studies of the corrosion by molten salts on stainless steels have also been made.[4]

The possibility of serious hot salt corrosion on nickel-base and other high-temperature alloys is of great interest where the alloys are to be used for such applications as missile skins. Various sources of contaminating salts would exist including finger marks, marine environments, and combustion products from missile fuels. It could be anticipated that any detrimental effect of the corrosion would be accentuated on thin sheet material inasmuch as corrosion to very slight depths would appreciably reduce the effective thickness of materials originally only several thousandths of an inch thick. The attack could also produce stress raisers that would lower the load-carrying capacity further. Notch effects would be particularly important for such notch-sensitive materials as Rene 41 and M-252.

Although there is little in the literature directly concerned with the hot salt corrosion of high-temperature alloys, useful related information can be noted. The Oak Ridge National Laboratory has reported on the corrosion of alloys by molten fluoride systems, mostly in the absence of air.[5, 6] The work indicated that protective films are fluxed away by molten fluorides. The selective removal of chromium from an alloy with consequent formation of subsurface voids was found to represent a characteristic molten salt corrosion phenomenon. Voids in Inconel caused by the selective removal of chromium in high-temperature oxidation tests were reported by Brasunas.[7] Various studies concerned with corrosion by oil ash and by vanadium pentoxide in particular have been

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Abstract

The corrosion of Inconel X, Inconel 702, Rene 41, M-252, and WF-11 (Haynes 25) by potassium chloride and lithium fluoride at 1600 to 1900 F was studied. Thin coatings of the salts (1.5 mg/cm²) caused severe corrosion of the alloys in air, which resulted in accelerated failures of thin sheet specimens in creep-rupture testing. Rankings for the alloys based on creep-rupture tests were similar for uncoated and salt-coated materials: WF-11, Rene 41, and M-252 best, Inconel 702 poorer, and Inconel X poorest.

The corrosion products consist mainly of oxides and spinels, and also contain small amounts of chromates. Only very little corrosion, if any, occures without oxygen. The presence of the salt prevents the normal formation of a protective oxide film. X-ray diffraction studies showed differences between the normal oxidation products and the oxide corrosion products produced with salt present.

The types of corrosion include severe surface attack, intergranular penetration, and internal void formation. All of the alloys were susceptible to each of these types of corrosion. Grain boundary separation effects due to stress (2,500 to 10,000 psi) were also found. 4.3.6, 6.3.10

published.[8, 9] In general, it is believed that the pentoxide fluxes the chromium oxide which would otherwise form a protective coating.

A standard test program involving the application of salts to thin sheet materials followed by exposure to elevated temperatures at various stress levels was performed to determine the severity of attack on Inconel X, Inconel 702, M-252, Rene 41, and WF-11 (Haynes 25). In addition, experimental studies directed toward developing an understanding of the mechanism of hot salt corrosion were performed, including both chemical and metallurgical studies.

Experimental Procedures and Results
Standard Test Program

Various alloys in the form of thin-sheet creep-rupture specimens, uncoated

Moskowitz **Redmerski**

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LAWRENCE REDMERSKI engages in work on stainless steels at Crucible Steel's Central Research Laboratory. He received a BS in metallurgical engineering from the University of Pittsburgh. He was employed at the Metals Research Laboratory of Carnegie Institute of Technology while attending college, and went directly to Crucible upon graduation in 1958. He is a member of ASM.

and coated with potassium chloride (KCl) or lithium fluoride (LiF) were exposed to selected high temperatures at sustained tensile loads. The temperatures chosen were from 1600 to 1900 F. The specimens were under sustained tensile loads of either 2,500, 5,000, or 10,000 psi while exposed at temperature, and were exposed to each temperature and stress level for a maximum of 30

TABLE 1—Chemistry and Thickness of Experimental Materials

Element	WF-11		Inconel 702	Inconel X	M-252	Rene 41
	0.016*	0.010	0.014	0.010	0.011	0.011
Al	.....	.....	3.54	0.76	1.25	1.45
B	.....	.....	.....	.....	0.004	0.006
C	0.06	0.11	0.05	0.04	0.13	0.05
Co	Bal.	Bal.	.....	0.12	9.76	10.94
Cr	20.73	20.01	15.76	15.12	18.63	19.22
Cu	.....	.....	0.07	0.06	.....	.....
Fe	2.16	2.42	0.31	6.83	0.30	0.54
Mo	.....	.....	.....	.....	10.02	9.81
Mn	1.50	1.56	0.04	0.62	0.07	0.02
Ni	9.68	9.99	79.43	72.65	Bal.	Bal.
P	0.007	0.009	.....	.....	.....	.....
S	0.007	0.010	0.005	0.007	.....	0.005
Si	0.61	0.63	0.17	0.34	0.10	0.11
Ta + Cb	.....	.....	.....	0.96	.....	.....
Ti	.....	.....	0.60	2.54	2.67	3.02
W	14.70	14.56	.....	.....	.....	.....

* Thickness, inches.

hours unless failure occurred earlier. The specimens were cut transverse to the rolling direction and preoxidized before being tested.

Materials. Five alloys currently of importance for high-temperature applications were chosen for the test program. Four of these alloys represent nickel-based materials containing 15 to 20 percent chromium for oxidation resistance and varying smaller amounts of aluminum and titanium for precipitation hardening. The fifth alloy, WF-11, represents a cobalt-base alloy which can be hardened by cold working rather than by aging.

The five alloys were obtained in the form of thin sheet in the mill-annealed condition. Table 1 shows the chemical compositions and thicknesses of the as-received materials. The thicker (0.016-inch) WF-11 was used in the test program, and comparison tests were performed with the thinner material (0.010-inch) when it later became available.

Preparation of Creep-Rupture Specimens. The as-received alloys were cut into strips, 5 by 1 inches, transverse to the rolling direction. The strips were then clamped into packs approximately 1 inch thick, and the creep-rupture specimens were milled from these packs (except for the packs of WF-11 on which grinding was used). Creep-rupture specimens having a 2-inch-long and 0.4-inch-wide reduced section were used.

A 360-grit finish was given to the reduced sections, after which the specimens were cleaned and degreased. A 16-hour treatment in air at 1350 F was then given to provide a thin, adherent, and uniform oxide coating for all the alloys. This preoxidation step also represents an aging treatment (precipitation hardening) for the four nickel-base alloys.

Small areas at the ends of the reduced sections were scraped clean of oxides for the later welding on of thermocouple wires, the hardness checks were also performed on these bare areas. The specimens to be salt-coated were placed flat on a polymethylmethacrylate panel, and covered with masking tape over all areas except for the reduced sections. The contaminating salt was applied to one side

TABLE 2—Results of Creep-Rupture Testing for Inconel X[a]

Test Temperature (°F)	2,500 psi			5,000 psi			10,000 psi		
	Uncoated	KCl	LiF	Uncoated	KCl	LiF	Uncoated	KCl	LiF
1600				Disc	Disc[b]	Disc	7.6[d]	11.3[b]	8.0[c]
1700	Disc	Disc	Disc	15.7[e]	8.9[c]	5.7	0.9[b]	0.5	0.9
1800	Disc	11.9[c]	9.7[b]	2.1	1.0	1.1	....	....	....
1900	Disc[b]	2.1[b]	5.6[d]	0.7	0.2	0.3	BOL	BOL	BOL

[a] BOL—specimen broke on loading.
Disc—specimen did not break in 30 hr so test discontinued.
[b] Average of two test results.
[c] Average of three test results.
[d] Average of four test results.
[e] Average of six test results.

TABLE 3—Results of Creep-Rupture Testing for Inconel 702[a]

Test Temperature (°F)	2,500 psi			5,000 psi			10,000 psi		
	Uncoated	KCl	LiF	Uncoated	KCl	LiF	Uncoated	KCl	LiF
1600						Disc	29.8	23.2[b]	15.7[c]
1700		Disc	Disc	Disc	Disc	16.4[b]	2.3[b]	1.6[b]	1.0[b]
1800	Disc	Disc	13.6	3.7	3.9	0.6	....	....	BOL
1900	Disc[b]	3.8[c]	2.5[b]	1.1[c]	0.2	0.2	0.1	BOL	BOL

[a] BOL—specimen broke on loading.
Disc—specimen did not break in 30 hr so test discontinued.
[b] Average of two test results.
[c] Average of three test results.

TABLE 4—Results of Creep-Rupture Testing for M-252[a]

Test Temperature (°F)	2,500 psi			5,000 psi			10,000 psi		
	Uncoated	KCl	LiF	Uncoated	KCl	LiF	Uncoated	KCl	LiF
1600	....	....	....	....	....	....	Disc	Disc	Disc
1700	....	....	....	Disc	Disc	Disc[b]	Disc	Disc	4.6
1800	Disc	Disc	Disc[b]	Disc	Disc	9.7[b]	2.9[c]	4.8[c]	0.1[b]
1900	Disc	Disc	0.7[b]	Disc	3.3[b]	0.3	0.3	0.2	BOL

[a] BOL—specimen broke on loading.
Disc—specimen did not break in 30 hr so test discontinued.
[b] Average of two test results.
[c] Average of three test results.

TABLE 5—Results of Creep-Rupture Testing for Rene 41[a]

Test Temperature (°F)	2,500 psi			5,000 psi			10,000 psi		
	Uncoated	KCl	LiF	Uncoated	KCl	LiF	Uncoated	KCl	LiF
1600	....	....	....	....	....	Disc	Disc	Disc	Disc[b]
1700	....	....	....	....	....	26.8	Disc	Disc	0.9
1800	....	....	15.8	Disc	Disc	2.0	8.5	6.6[b]	0.6
1900	Disc[b]	Disc	0.9[c]	11.4[b]	2.1[b]	0.1[b]	0.2[b]	0.2[b]	BOL

[a] BOL—specimen broke on loading.
Disc—specimen did not break in 30 hr so test discontinued.
[b] Average of two test results.
[c] Average of three test results.

TABLE 6—Results of Creep-Rupture Testing for WF-11[a]

| | TIME TO FAILURE (hr) | | | | | | | | |
| | 2,500 psi | | | 5,000 psi | | | 10,000 psi | | |
Test Temperature (°F)	Uncoated	KCl	LiF	Uncoated	KCl	LiF	Uncoated	KCl	LiF
1600	....	....	....	....	....	....	Disc	Disc	Disc
1700	....	....	Disc[b]	.... (Disc)	.... (Disc)	Disc (Disc)	Disc[b] (Disc[b])	28.0[b] (22.0[b])	6.6 (5.8)
1800	Disc	Disc[b]	Disc. (8.3[b])	Disc (Disc)	Disc (Disc)	11.0[b] (2.8[c])	8.4[b] (6.5)	3.4[b] (1.6)	1.6 (0.9)
1900	Disc	Disc (Disc)	9.7[d] (3.7)	25.6 (29.6)	29.0[b] (11.1[b])	3.0 (1.3)	0.8[b]	0.2	0.2

- BOL—specimen broke on loading.
  Disc—specimen did not break in 30 hr, so test discontinued.
  Figures in parentheses are for 0.010-inch-thick WF-11, other figures are for 0.016-inch-thick WF-11.
[b] Average of two test results.
[c] Average of three test results.
[d] Average of four test results.

only on the reduced section. Potassium chloride was applied by spraying on a hot concentrated aqueous solution with a fine chromatographic sprayer. Lithium fluoride was applied by brushing on a suspension of finely powdered chemical in reagent acetone, the mixture being constantly agitated to keep the LiF in suspension. Both methods of application provided a fairly uniform thin salt coating with sufficient adhesion to allow necessary handling.

The creep-rupture specimens were weighed before and after being coated, and a coating of 8 ± 2 mg (1.5 mg/cm²) was considered to be satisfactory. With even coverage, no appreciable water content, and the assumption of theoretical density, an 8-mg coating of KCl on the reduced section gives a calculated thickness of 0.00031 inch. The calculated thickness for the 8-mg LiF coating is 0.00024 inch.

Finally, thermocouples were welded to the bare metal at both ends of the reduced section on the uncoated side for temperature measurements during testing.

Creep-Rupture Testing. The specimens were mounted in the creep-testing equipment, using previously scribed reference marks on the grips and on the creep units to ensure perfect alignment and absence of torque stresses. Separate furnaces were reserved for use with uncoated, LiF-coated, or KCl-coated specimens to avoid contamination problems.

A very light load (500 to 600 psi) was placed on the specimens during heat-up to maintain slight tension and avoid buckling difficulties. Heat-up times were kept between 2 and 3 hours. When the specimens reached the desired temperature, a soaking time of 15 to 20 minutes was allowed, after which the selected stress was applied and the time period begun. The test temperatures were maintained within 5 to 10 degrees F of the selected temperatures.

When specimens broke within the specified time period, an automatic shut-off switch cut the power into the furnace. The specimens which did not break within the test period were permitted to cool under stress and removed for examination. Elongation measurements were made using previously placed punch marks and scribed lines. The degree of damage done to unbroken specimens was

TABLE 7—Chromium Content of Corrosion Products and Corroded Metal (Potassium Chloride Attack)[a]

| | CHROMIUM ANALYSES (PERCENT) | | |
Alloy	As-Received Alloy	Corrosion Product	Residual Metal
Inconel X (I)	15.04	14.15	13.55
M-252	18.63	23.97	15.78
0.016-inch WF-11	20.7	16.27	19.19

[a] Specimens coated in the as-received condition with KCl, and placed in a furnace at 1600 F for 16 hours.

evaluated by room-temperature tensile testing or metallographic examination.

Tables 2 to 6 show the results obtained in the standard test program performed on the five alloys.

Collection and Analyses of Corrosion Products

Specimens 5 by 1¾ inches were coated on one side with about 60 mg of salt per square inch. The thick KCl coatings were obtained by repeatedly spraying on the solution and drying the specimen. The thick LiF coatings were obtained by brushing on a heavy suspension of LiF in acetone. The specimens were placed flat on a porcelain tray (coated side up) and put unstressed into a furnace for 16 hours at 1600 F. The specimens were quickly placed in beakers upon removal from the furnace so that the corrosion products flaking off on cooling would be collected. A voluminous and nonadherent mass of corrosion product was formed on the salt-coated side of all the alloys as a result of the hot salt corrosion.

The KCl corrosion products for preoxidized (prior to salt coating) and not preoxidized specimens were found to be identical by spectrographic and X-ray diffraction. The qualitative spectrographic results showed chromium and nickel as major constituents (cobalt also for WF-11), with other elements present related to alloy composition. The phases identified in the samples by X-ray diffraction were as follows, with the major constituent underlined:

Inconel X	—	NiO + Spinel
		+ Fe₂O₃ — type oxide
Inconel 702	—	NiO + Spinel
		+ Fe₂O₃ — type oxide
M-252	—	NiO + Spinel
		+ Fe₂O₃ — type oxide
WF-11	—	CoO · 3NiO
		+ Spinel + Co₃O₄
Rene 41	—	NiO + Spinel
		+ Fe₂O₃ — type oxide

The spinels listed above have struc-

tures similar to that of Fe_3O_4 but with a smaller cell size and lattice parameters of 8.27 Å compared to the Fe_2O_3 parameter of 8.38 Å.

To study the products of KCl corrosion further, both corrosion product and corroded metal resulting from attack on Inconel X, WF-11, and M-252 were subjected to quantitative chemical analysis for chromium content. Standard "wet" methods were used, and the results for total chromium are shown in Table 7. Minor amounts of soluble chromium (chromates) ranging from 0.06 percent for the WF-11 to 0.4 percent for the M-252 were found in the KCl-corrosion products for all five alloys.

The corrosion products resulting from LiF attack (specimens not preoxidized) were present mainly as green or black flaky materials. Spectrographic analysis showed compositions similar to those resulting from KCl attack. Wet analysis showed minor amounts of soluble chromium (approximately 0.1 percent) for all the LiF products. The phases identified in the samples by X-ray diffraction were as follows, with the major phases underlined:

Inconel X	—	MO + LiF
		+ Cr₂NiO₄ (trace)
Inconel 702	—	MO + LiF
		+ Cr₂NiO₄
M-252	—	MO + Cr₂NiO₄
		+ Fe₂O₃ — type oxide (trace)
WF-11	—	Co₃O₄ + LiF + NiO
		+ Cr₂NiO₄ (trace)
Rene 41	—	MO + LiF
		+ Cr₂NiO₄

Variations of lattice parameter were observed among the MO-type oxides listed above. The patterns indicated the structure of NiO, but cell sizes varied slightly between samples.

Specimens of each of the alloys were also given an oxidation treatment of 16 hours at 1600 F without salt present and samples of the oxides resulting ("normal oxides") were taken by a parlodion film stripping technique for X-ray diffraction analysis. The samples were found to con-

Figure 1—Corrosion of specimens of M-252 coated with lithium fluoride and tested at 1900 F under a stress of 2,500 psi (100X)

Figure 2—Corrosion of Specimens of Inconel 702 coated with lithium fluoride and tested at 1900 F under a stress of 2,500 psi (100X)

tain the following phases, with the major phases underlined:

Inconel X — Spinel + Cr_2O_3
Inconel 702 — Cr_2O_3 + Spinel
M-252   — Spinel + aFe_2O_3
               + $NiMoO_4$ (trace)
WF-11   — Cr_2O_3 + Spinel
Rene 41 — Spinel + $NiMoO_4$
               + Fe_2O_3 (trace)

The spinels existing in these samples could be such compounds as Fe_2NiO_4, Cr_2FeO_4, Fe_2CoO_4, Cr_2NiO_4, and others, They have lattice parameters of approximately 8.34 Å, except for Inconel 702 at 8.28 Å.

Effects of Varying Salt Thickness

Tests were performed to obtain information on the effects of varying the quantity of contaminating salt applied before creep testing, since the thicknesses of salt coatings used in the test program were chosen in an arbitrary manner. On the basis of prior results, Inconel 702 was chosen for testing with KCl and with LiF at 1900 F and 2500 psi, and WF-11 was tested with LiF at 1900 F and 5000 psi. All specimens were weighed before and after being coated, and were then tested by standard method. The times to fracture for the varying quantities of salt are shown in Tables 8 and 9.

Effects of Stress

Tests were performed on salt-coated specimens in the creep-rupture equipment with and without the application of stress, the conditions being otherwise identical. The conditions chosen were such that none of the specimens would break in the creep testing furnace. Duplicate tests were run so that one set of tested specimens could be tensile tested at room temperature and another set used for metallographic examination. Table 10 gives the treatment of the materials and their subsequent tensile strength and elongations. Metallographic studies of longitudinal sections normal to the sheet did not show significant difference in corrosion related to the presence or absence of stress.

Creep-Rupture Tests in an Argon Atmosphere

Creep-rupture tests were performed on salt-coated specimens in an argon atmosphere to obtain information on the extent of corrosion occurring in the absence of oxygen. The preparation and loading of the specimens were the same as for the standard tests in air. The specially adapted furnace was purged overnight with argon before each run with the specimen mounted inside, and a slow flow

TABLE 8—Effect of Salt Thickness on Creep-Rupture Time for Inconel 702[a]

Weight of LiF (mg/cm²)	Time to Rupture (hr)	Weight of KCl (mg/cm²)	Time to Rupture (hr)
0.0	Disc[b]	0.0	Disc[b]
0.18	Disc[b]	0.16	Disc[b]
0.29	2.4	0.64	8.7
0.60	1.8	1.1	7.7
1.1	1.7	1.5	4.6
1.5	2.0	2.1	2.7
2.2	1.4	3.6	3.2
4.7	0.8	10.2	5.0
13.1	0.9		

[a] Testing conditions: 1900 F under a stress of 2,500 psi.
[b] Test discontinued at 30 hours without failure.

TABLE 9—Effect of Lithium Fluoride Thickness on Creep-Rupture Time for 0.016-Inch WF-11[a]

Weight of LiF (mg/cm²)	Time of Rupture (hr)
0.0	Disc[b]
0.27	9.6
0.55	7.9
0.98	3.7
1.5	2.0
1.9	0.7
4.5	0.8
12.5	1.4

[a] Testing conditions: 1900 F under a stress of 5,000 psi.
[b] Test discontinued at 30 hours without failure.

of argon through the furnace was maintained during testing. The test conditions were such that severe corrosion and accelerated failure would be encountered if air were present.

Table 11 shows the results obtained in argon as well as the results obtained in air with the same alloy, stress, salt, and temperature conditions in the standard test program. Figures 1 and 2 show photomicrographs of the alloys after the creep testing in argon. The photomicrographs represent unetched longitudinal sections normal to the sheet, with the top surface having been the salt-coated one.

Metallographic Studies

Metallographic examinations were made on numerous specimens, both uncoated and salt-coated, which had been creep-rupture tested. Coupons approximately ½ inch long were cut from the creep specimens, When the specimen had failed during testing, the coupon was taken with the fractured zone as one end. When the specimens had not failed, the coupons were taken from the center of the reduced section. The coupons then represent longitudinal sections normal to the sheet taken along the edge of the creep specimen, and when polished will still show the original coated surface, uncoated surface, and failure. The coupons were so taken that the polished surfaces would represent areas at least ⅛ inch from the original edge of the creep specimen. The coupons were coated with an epoxy resin to preserve the edges during polishing, and were mounted and polished by standard procedures. Most of the corrosion information was provided by unetched specimens.

Figures 3 to 5 show representative corrosion effects. The photomicrographs represent longitudinal sections normal to the sheet, with the top surface having been the salt-coated one. The specimens are unetched unless otherwise noted. Figure 3 shows photomicrographs made near the point of fracture on Rene 41 specimens which had been tested at 1900 F under a stress of 5000 psi. Figure 4 shows WF-11 after corrosion by KCl, the cross section having been etched by modified aqua regia. Figure 5 shows internal holes produced in Inconel 702 by KCl attack at 1600 F as they appear at different magnifications. Figure 6 shows microcracking (stress-induced voids, largely at grain boundaries) produced in Inconel 702 by creep testing at 1600 F and 10,000 psi.

The metallographic examinations showed various types of corrosion occurring, including intergranular penetrations inward from the surface, general attack over the surface involving considerable metal removal, and holes inside the metal with no apparent connection to a surface. The examination of a wide variety of creep-rupture specimens showed all the alloys to be susceptible to all three of these types of corrosion.

Both the internal holes and the penetrations were observed, usually to a relatively mild degree, for all the alloys creep tested without any salt coating. Low-magnification study of the surfaces
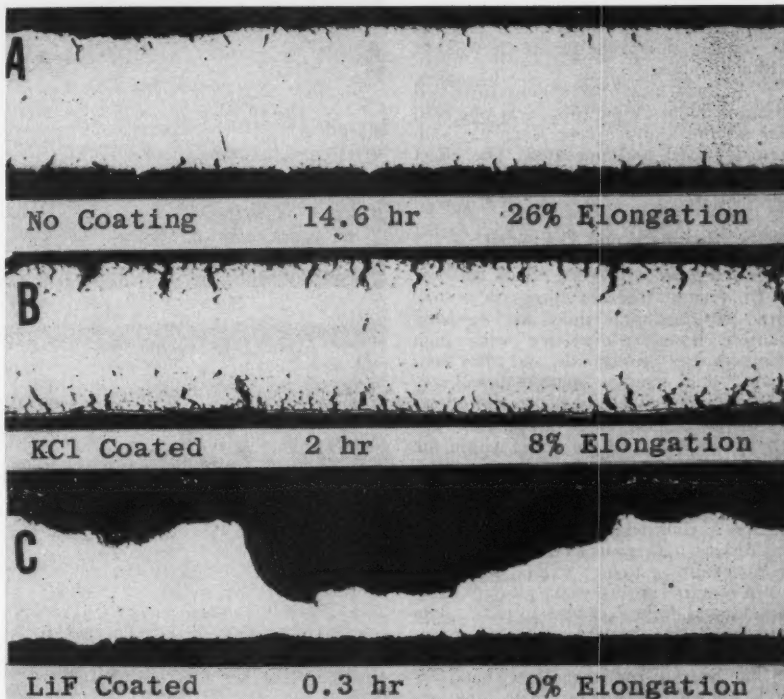
Figure 3—Photomicrographs near fracture point of Rene 41 tested at 1900 F under a stress of 5,000 psi (75X)
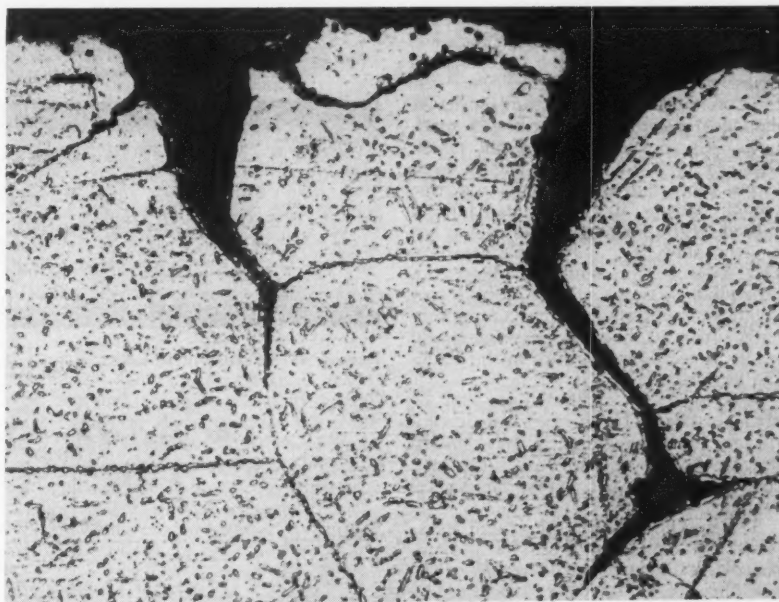
Figure 4—Intergranular penetration on a specimen of WF-11 coated with potassium chloride and creep-rupture tested at 1900 F under a stress of 10,000 psi (750X). Etched by nitric acid-hydrochloric acid mixture.

TABLE 10—Tensile Tests on Specimens Stressed and Unstressed During Prior Hot Salt Corrosion[a]

Alloy	Coating	Stress During Corrosion (psi)	Tensile Strength (psi)	Elong. in 2 Inches (Percent)
Inconel X	KCl	none	89,000	9.0
		5,000	84,000	2.5
Rene 41	LiF	none	92,000	2.0
		10,000	102,000	1.0

[a] Coated specimens were held for 30 hours at 1600 F and under stresses shown prior to room-temperature tensile tests.

of some of the uncoated specimens after creep testing also showed clear patterns of shallow intergranular attack without grain dropping.

"Microcracking," or stress-induced grain-boundary separation, was observed for all the alloys except Rene 41, both tested coated and uncoated. The effect was most prevalent in the Inconel X and Inconel 702.

Summary and Discussion

Test Program

In general, the test program results are consistent and show the expected shorter times to failure with high temperatures (stress, salt, and alloy constant) and stresses (temperature, salt, and alloy constant). The corrosive effects of LiF produced accelerated creep-rupture failures for all the alloys within the time limitations of the test program. Potassium chloride also produced accelerated failure for all the alloys, but under a considerably smaller range of conditions. In general, more severe temperature and/or stress conditions were required with a given alloy to show accelerated failure caused by KCl, thus indicating the greater severity of corrosion provided by LiF.

The over-all results indicate that 1600 F is too low a temperature to show accelerated failure within the specified 30-hour test period. This in itself does not mean that considerable corrosive damage might not have occurred. It could be expected that in many instances accelerated failures of the coated specimens would be encountered were the tests continued to failure, and corrosive damage to unbroken creep-tested specimens was shown by subsequent tensile tests. At 1900 F under the higher stress levels, rapid failure is encountered even without salts, so that accelerated failures caused by the salts cannot be shown. For a given alloy, it is only at temperatures and stresses representing a region intermediate between very mild and very severe conditions for the uncontaminated material that salt corrosion would result in accelerated failure in the standard test program.

A comparison of the alloys can be made based on high-temperature creep-rupture life as measured in the standard program for the uncoated and salt-coated conditions. Table 12 shows the general rankings so derived.

The rankings for the salt-coated specimens are similar to those for the uncoated specimens. The differences, whatever they might be, that exist among the alloys in their relative susceptibility to the salt corrosion are not sufficient to provide a significant change in the ranking of coated alloys as compared with that of uncoated alloys.

It should be emphasized that the rankings apply only to the results of the creep-rupture tests with the testing conditions as specified and with the alloys having been given the described, not-necessarily-optimum, heat-treatments.

Analyses of Corrosion Products

The spectrographic and X-ray diffraction results for the KCl-attack specimens
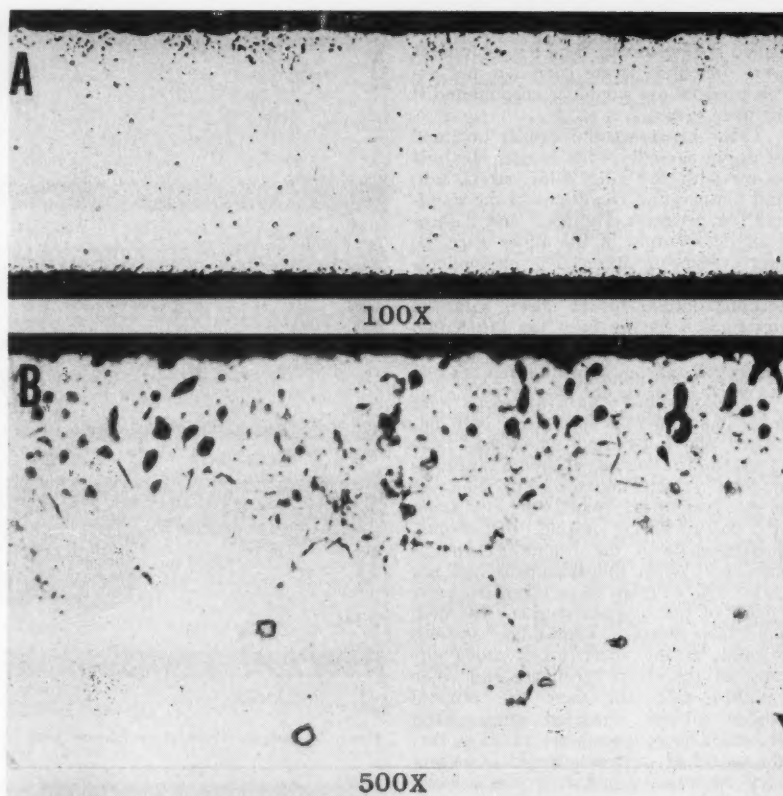
Figure 5—Internal holes produced in potassium chloride-coated Inconel 702 by creep testing at 1600 F under a stress of 10,000 psi (18.9 hr)
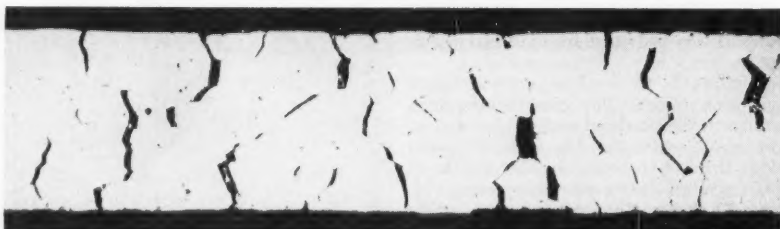
Figure 6—Microcracking (stress-induced voids) in uncoated Inconel 702 tested at 1600 F under a stress of 10,000 psi (75X)

TABLE 11—Creep-Rupture Tests For LiF-Coated Specimens (Argon versus Air)[a]

Alloy	Temperature (°F)	Stress (psi)	TIME TO FAILURE (hr)	
			Argon	Air
Inconel X	1800	2,500	10.8	9.7
Inconel 702	1900	2,500	Disc	2.5
M-252	1900	5,000	Disc	0.3
0.016-inch WF-11	1900	5,000	17.9	3.0
0.010-inch WF-11	1900	5,000	13.0	1.3
Rene 41	1900	5,000	4.6	0.1

[a] Disc—test discontinued after 30 hours without failure.

showed the corrosion products to be primarily nickel oxides and chromium oxides not containing an appreciable quantity of the contaminating salt. No significant difference was shown in the corrosion product composition resulting from the specimens being preoxidized or not preoxidized before the attack.

Quantitative analyses for chromium

were performed on corrosion products and residual metal after KCl attack at 1600 F on three of the alloys. The alloy containing 18.63 percent chromium, M-252, would provide an oxide corrosion product containing approximately 14.0 percent chromium if all the alloy constituents moved proportionately into the oxide layer. The chromium analysis

TABLE 12—Relative Ranking of Alloys Based on Creep-Rupture Tests[a]

No Salt	KCl-Coated	LiF-Coated
M-252	M-252	M-252
WF-11	WF-11	WF-11
Rene 41	Rene 41	Rene 41
Inconel 702	Inconel 702	Inconel 702
Inconel X	Inconel X	Inconel X

[a] Best alloy on top, bracketed alloys about equal.

of 23.98 percent therefore represents a very strong enrichment of chromium in the oxide layer. The chromium content of the residual metal at 15.78 percent is appreciably below the 18.63 percent figure for the metal before corrosion. Inconel X corrosion product would contain approximately 11.5 percent chromium were all the alloy constituents present in the same proportion as in the alloy. The analysis of 14.15 percent chromium therefore represents an enrichment of chromium, though to a lesser degree than for the M-252. The metal after corrosion shows a lower chromium content than it did as received. The WF-11 corrosion product would contain approximately 15.8 percent chromium were all the alloy constituents present proportionately. The actual figure of 16.27 percent chromium indicates no appreciable enrichment in chromium. The metal after corrosion is somewhat lower in chromium content, but the difference is the least among the alloys tested.

Since the selective removal of chromium from the alloy matrix represents a possible mechanism for the formation of internal holes, the correlation of the chromium analysis in the corrosion products with the results shown by metallographic examination is of interest. The metallographic specimens prepared from the creep specimens which had been tested with KCl at 1600 F showed the major corrosive effect for M-252 and for Inconel X to be the formation of internal holes; the WF-11 showed only a small number of shallow intergranular penetrations and none of the internal holes.

A detailed comparison of the X-ray results for the corrosion products resulting from the different conditions (uncoated, KCl-coated, and LiF-coated) is of interest to indicate whether different corrosion products are obtained. Within the limitations of the X-ray diffraction data, the following general statements can be made:

(1) The normal oxidation products consisted largely of spinels (Fe_3O_4-type structure) and Cr_2O_3 (with probably some substitution of other cations for Cr). No appreciable quantity of MO-type oxide was found.

(2) The KCl corrosion products consisted largely of spinels, NiO, and the Fe_2O_3-type oxide. The spinels were different from those found in the normal oxidation product, as shown by the different lattice parameters.

(3) The LiF corrosion products consisted largely of MO-type oxide, and did not contain an appreciable quantity of M_2O_3-type oxide.

The findings above show that there were considerable differences in the characters of the oxides formed. The corrosion products from the salt-coated specimens all contained appreciable quantities of MO-type oxide (mainly NiO for the KCl corrosion products, more substitution of other cations for Ni for the LiF corrosion product), which was not found in the normal oxidation products. The LiF corrosion products did not contain any appreciable quantity of M_2O_3-type oxide, which was an important constituent of the normal oxidation products. Also, the spinels formed in normal oxidization were different from those formed with salts present.

The relatively small quantities of chromates found in the corrosion products probably result from a reaction involving chromium (or chromium oxide), contaminating salt, and oxygen.

Effects of Varying Salt Thicknesses

The tests involving the application of varying quantities of salt indicate that the time to failure is dependent on the amount of salt. Considerable damage can be done by relatively small quantities of salt. There is a trend toward quicker failure with heavier salt deposits, and there is a leveling off in the degree of acceleration of failure at the highest salt quantities tested. Comparison of the results for the KCl and the LiF coatings on Inconel 702 indicates a greater degree of corrosivity for the LiF.

The results seem to indicate that the quantity of salt coating chosen for the program represents an intermediate amount of contaminant and that minor increases or decreases in quantity of salt would not make for greatly different results.

Test in Argon Atmosphere

Both the creep-rupture test results and the metallographic studies indicate that the major corrosive effects caused by LiF in air are not produced in an argon atmosphere. Microcracking related to the stress represents the major detrimental effect noted for the specimens tested in argon. Some specimens also showed shallow intergranular penetrations. This effect could possibly result from oxidation which occurred during the preoxidation step, or from contaminating oxygen in the argon atmosphere.

Metallographic Studies

The salt-coated specimens were in general severely corroded; the corrosion usually showed on both sides of the specimen but to a greater degree on the coated side. The metallographic studies showed various types of corrosion occurring, including penetrations inward from the surface, general attack over the surface involving considerable metal removal, and holes inside the metal with no apparent connection to any surface. As shown by etched specimens the penetrations in general are intergranular in nature, a fact which is also apparent even in the examination of numerous unetched specimens. Both KCl and LiF produced

all these types of corrosion. The general surface attack is however associated more frequently with attack by the LiF. The internal holes have been observed both for stressed and unstressed specimens, and so do not appear to represent a stress effect. The majority of holes tend to be clustered not too far from the salt-coated surface. The WF-11 appeared to be less affected by the "hole" type corrosion than the other alloys.

None of the alloys was immune to any of the above-mentioned forms of corrosion.

Conclusions

(1) All of the alloys in the test program are seriously corroded in air in the presence of molten KCl or molten LiF. A test program provided quantitative data on the time-to-failure of the alloys (thin sheet specimens) with and without thin salt coatings (1.5 mg/cm^2) under various temperature and stress conditions. General rankings for the alloys based on the creep-rupture tests were similar for uncoated and salt-coated materials, showing M-252, WF-11, and Rene 41 best, Inconel 702 poorer, and Inconel X poorest. The two salts are about equal in accelerating failure of Inconel X, but LiF causes more rapid failure for the other alloys.

(2) The over-all chemistry of the salt corrosion is such that the corrosion products consist mainly of oxides and spinels, and also contain small amounts of chromates. Only very little corrosion if any occurred without the presence of oxygen.

(3) The presence of KCl or LiF prevents the normal formation of a protective oxide film. The precise mechanism through which the salt "fluxes" the oxide films is not known, but might involve the intermediate formation of complex compounds which decompose to oxides and spinels producing a nonprotective, nonadherent, and voluminous mass of corrosion product. Differences in X-ray diffraction patterns between the normal oxidation products and the salt-produced oxide corrosion products have been found, with the former showing M_2O_3-type oxides and spinels and the latter showing MO-type oxides. Although only small quantities of chromates were found, their presence indicates a possibly important reaction involving chromium (or chromium oxide), salt, and oxygen.

(4) Structurally, corrosion was found to occur in the following three forms: severe surface attack with consequent metal removal and complete perforation of thin sheets in a short time, intergranular penetrations into the metal, and internal (subsurface) voids formed in the alloy. All of the alloys were susceptible to each of these types of corrosion.

(5) The general surface attack and the intergranular penetrations both appear to be manifestations of oxidation reactions. The grain boundaries will in general represent favorable paths for the oxidation attack. Under the most severe conditions, the very rapid general attack could tend to prevent manifestation of the intergranular attack.

(6) Correlation was found between the formation of internal holes and a chromium enrichment in the corrosion products. This finding is in agreement with previous reports that such holes may be due to the precipitation of vacancies left by the diffusion of chromium to the surface where it is being preferentially oxidized.

(7) The three forms of corrosion described can seriously weaken a thin sheet material operating under stress both by reducing the effective thickness and by introducing detrimental notch effects. Rapid failure of materials under stress can then be encountered. Other effects of stress on the corrosion, aside from grain-boundary separation effects which are not connected with contaminating salts, were not indicated. It is believed that the rapid failures under stress caused by the salts do not represent stress corrosion but rather the breaking by stress of materials seriously weakened by corrosive attack.

(8) The results of creep-rupture tests on specimens coated with varying quantities of salts indicate that the amount of salt does affect the time to failure, that considerable damage can be done by relatively small (0.3 mg/cm^2) quantities of salt, and that there is a leveling off in the degree of acceleration of failure at the higher salt quantities tested (2 to 12 mg/cm^2).

Acknowledgment

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Any discussion of this article not published above will appear in December, 1961 issue.

NATIONAL ASSOCIATION of CORROSION ENGINEERS

Chlorosulfonated Polyethylene (Hypalon)

A Report of NACE Technical Unit Committee T-6A[1]
On Organic Coatings and Linings for Resistance to
Chemical Corrosion; Prepared by Task Group T-6A-18[2]
On Chlorosulfonated Polyethylene

NACE TECHNICAL COMMITTEE REPORT
Publication 61–3

Foreword

COMMITTEE T-6A was organized for the purpose of assembling and disseminating to the corrosion engineer, factual and quantitative data on the performance and limitations of the various organic materials that are successfully used in coatings and linings. While every attempt is made to be factual in the coverage of application and chemical resistance tables and physical properties, it nevertheless should be recognized that changes in compounding formulations of organic materials for coatings or linings enhance or detract from their inherent corrosion resistance characteristics. Under such circumstances, these reports and recommendation lists must be viewed as showing average properties only. The possibility of changes in chemical and physical characteristics as produced by various manufacturers or applicators of the material should be kept in mind.

Definition

Chlorosulfonated polyethylene* is the product of reacting polyethylene with chlorine and sulfur dioxide.[1] This chemical modification changes thermoplastic polyethylene into a synthetic elastomer which when compounded with curing ingredients and accelerators can be vulcanized into elastomeric products[2].

The properties of CSPE depend to a large extent on the amounts of chlorine and sulfur present. However, the commercial grades are similar enough in composition and resistance to chemical corrosion that all three are covered by this report. Choice between these types can be referred to the manufacturers or applicators as this choice is based on method of application more than service desired. The polymer as supplied requires com-

pounding to obtain optimum properties for a specific use.[3]

Use and Summary of Properties

Like other elastomeric materials, the physical properties of CSPE can be varied over a wide range by compounding. In general it finds use in applications where combinations of the following requirements are found:

1. Resistance to swell by aliphatic oils

2. Resistance to ozone attack

3. Resistance to abrasion

4. Resistance to chemicals, particularly oxidizing chemicals

5. Resistance to color change on exposure to sunlight

6. Retention of physical properties on extended exposure to weathering

7. Retention of physical properties after heat aging

Forms Available

The raw polymer has the following physical characteristics:

Appearance: White, irregularly shaped chips.
Specific Gravity: 1.10.
Storage Stability: Excellent under the usual conditions prevailing in factory storage.
Health Hazards: None.
Solvents: Dissolves in such solvents as toluene, zylene, benzene, carbon tetrachloride, and mixtures of these solvents with alcohol,[4] naphtha, or ketones.

Compounded CSPE is available from various suppliers as:

1. Cured flat sheets and molded or extruded shapes (not covered in this report).

2. Uncured sheets for lining tanks or covering other objects (high temperature curing necessary).

3. Solvent based coatings used for coating objects by brush, roller or spray technique. (Such coatings are normally self-curing at room temperature.)

Effect of Compounding

The physical properties of cured films or sheets can be varied by changes in compounding ingredients. Of chief importance is the type of curing ingredient

Abstract

Physical and chemical properties of chlorosulfonated polyethylene are reported in detail. Topics discussed include uses, forms available, effects of compounding, effects of aging, abrasion and impact resistance, electrical properties, heat and weather resistance, priming, and application methods. Chemical resistances are reported at room temperature or at temperatures ranging from 158-212 F for chlorosulfonated polyethylene in 274 different media. These test media include alcohol and water, alkalies, gases, inorganic acids, oxidizing agents, chlorine dioxide, chrome plating solution, hydrogen peroxide, nitric acid, pickling solution, sodium hypochlorite, sulfuric acid, oils and solvents.   6.6.8, 5.4.5

used. In most cases optimum chemical resistance can be obtained with litharge (an organic lead complex is used in paints). In some instances where little or no water is present, as in concentrated sulfuric acid, etc., magnesium oxide should be used.

The rate of reaction of these curing ingredients can be varied by the use of organic accelerators to fit specific conditions. The supplier of the compounded material should be consulted concerning such requirements.

Other compounding ingredients play an important role in physical properties of CSPE as in other elastomers. The amount and type of such materials as antioxidants, fillers, softeners and tackifiers, extenders, colors, lubricants, and other elastomers and some plastics used in CSPE should be a function of the job the lining or coating is to perform. The exact compound can best be determined by the supplier of compounded material who is in possession of the facts about conditions of application and the exposure environment involved.

Physical Properties of Applied Coatings and Linings

As previously stated, the properties of various compounds of CSPE differ. In this report it will be assumed that proper compounding principles are followed for each specific exposure.

To round-out the picture, many physical properties are mentioned below, although they may not apply directly to linings and coatings.

[1] L. S. Van Delinder, Union Carbide Chemicals Co., South Charleston, W. Va., chairman.
[2] John R. Galloway, E. I. du Pont de Nemours and Co., Inc., Houston, Tex.; D. J. Kelly, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.; R. McFarland, Hills-McCanna Co., Carpentersville, Ill.; F. J. Ploederl, Wisconsin Protective Coating Co., Greenbay, Wisc.; B. Mohr, Ralph V. Rulon, Inc., Philadelphia, Pa.

* Hereafter referred to simply as CSPE. Du Pont is the sole supplier of the raw polymer under the tradename of Hypalon.

Effect of Aging

Under severe conditions (e.g., 300 days at 200 F) degradation of CSPE due to aging is accompanied by an increase in hardness, a reduction in ultimate elongation, and an increase in modulus.

Abrasion and Impact Resistance

CSPE vulcanizates are non-brittle elastomeric products capable of absorbing tremendous shock loads without failure. Abrasion resistance, as in most elastomers with high physical strength properties, is excellent and depends to a large extent on hardness and compounding.

Electrical Properties[4, 5]

Typical properties are as follows:

DC Resistivity, ohm-cm................10^{12}-10^{14}
Dielectric Constant 5-7
Power Factor 0.02-0.03
Dielectric Strength, volts/mil............400-750
Surface Resistivity, ohms.................10^{13}
Specific Insulation Resistance (K-Factor)..22,000
Insulation Resistance, 3/64" Wall
    #14 AWG, megohms/1000 ft...........5,600

Flame Resistance

Due to the high chlorine content, uncompounded CSPE does not support combustion. The compounding ingredients used will determine the degree of flame resistance in the vulcanizate.

Hardness

CSPE stocks can be compounded in hardness ranges from 35 Shore A to 98 Shore A. The most practical range is 60-85 Shore A.

Heat Resistance[6, 7, 8, 9]

The following table shows time required to reduce elongation of a CSPE vulcanizate to 100 percent elongation at various temperatures. This elongation is sometimes considered a good criterion of limit of serviceability.

Time to Reduce

Elongation to 100%	Temperature
10 hours	380 F
200 hours	300 F
2,000 hours	240 F
8,000 hours	200 F

As a CSPE vulcanizate heat ages, hardness characteristically increases.

Low Temperature Properties

A brittle point as low as —65 F can be obtained. Cured compounds normally start to stiffen at around 0 F, but flexibility can be obtained as low as —40 F by compounding.

Weather Resistance

Weathering of elastomers is a combination of attack by ozone, oxygen, and sunlight. CSPE is unaffected by ozone. Oxygen bomb tests show that the rate of oxidation is normally very slow. However, in the presence of ultraviolet light, the rate of oxidation is greatly accelerated. Therefore, to obtain long outdoor service, it is necessary to protect vulcanizates by absorbing or screening out ultraviolet light. This protection can be readily obtained by including in the CSPE compound pigments known by the rubber, plastics, and paint industries to be effective ultraviolet screening agents

(i.e., titanium dioxide, carbon black, some color pigments, etc.). Properly compounded vulcanizates have shown negligible change after as long as four years outdoor exposure in Delaware, California, and Florida.

Ozone Resistance[10]

No CSPE product has ever been known to fail due to ozone attack regardless of stress, temperature, or ozone concentration.

Toxicity, Color and Odor

The compounding ingredients will have more effect on color, odor, and toxicity imparted to materials in contact with a coating or lining than the polymer has.

General Comments on Chemical Resistance

Alcohol and Water

Properly vulcanized stocks cured with litharge show negligible swell. Magnesia cured stocks may swell up to 37 percent in 7 days at 158 F.

Alkalies

Resistance of CSPE to strong and weak alkalies is excellent. No failures have come to the attention of this committee.

Gases

Gas permeation of CSPE is low. It is in the same order of magnitude of neoprene at room temperature and approaches butyl at 200 F.

Inorganic Acids

There is little or no effect noticed on CSPE when exposed to hydrofluoric, or hydrobromic acids up to 158 F. Hydrochloric acid at 37 percent and 158 F has little or no effect, but HCl may permeate the lining and cause failure of the adhesive system. Field tests are recommended for the latter exposure.

Oxidizing Agents

There are seven materials in this category that are of wide interest. CSPE exhibits properties superior to many other elastomeric materials, but changes in concentration and temperature may make CSPE very satisfactory in one case and unsatisfactory in another. Specific limits are difficult to incorporate in a summary table and, therefore, experience in each chemical is shown here.

Chlorine Dioxide

Evidence to-date shows that CSPE stands chlorine dioxide better than any other elastomer but field results vary. Contamination by chlorine appears to be detrimental. Intermittent service seems to show disproportionate improvement in service life. Any recommendation should be qualified by a field test before large scale installation.

Chrome Plating Solution

Chrome plating solutions contain from 28 percent to 50 percent chromic acid and a small amount of sulfuric acid. At 158 F standard laboratory test temperature, CSPE lasts 5 months in 28 percent chromic acid and 1 month in 50 percent

chromic acid. Actual service temperature in plating industry is 125 F maximum. CSPE lined tanks and plates have been in service for two to four years. The actual time limit at service temperature is not known.

Hydrogen Peroxide

CSPE does not seem to be affected by 90 percent hydrogen peroxide at room temperature. Like any organic material, it affects the rate of oxygen loss and cannot be recommended in service where prolonged contact is experienced.

Nitric Acid

Experience has shown that CSPE should not be used in nitric acid service at any concentration if the temperature is above 150 F. A maximum temperature of 100 F, and a maximum concentration of 30 percent nitric acid are good limits. Above 30 percent, room temperature service only should be considered and then a field test is advisable. In fuming nitric acid, CSPE is attacked less rapidly than many other elastomers but service life is in the range of only 18-24 hours.

Pickling Solution

Pickling solutions used are 15 percent to 20 percent nitric acid and 3 percent to 4 percent hydrofluoric acid. HF has little or no effect on CSPE. Pickling solution has the same effect as nitric acid and generally cannot be used because normal service temperatures of approximately 150 F exceed the maximum recommended temperature of 100 F.

Sodium Hypochlorite

At some temperature higher than room temperature, CSPE linings will flake off in sodium hypochlorite. Whether this interferes with service life is a function of rate, which seems to be dependent on temperature and concentration. It seems safe to say that CSPE is satisfactory in 20 percent sodium hypochlorite at room temperature. Field tests should be conducted if higher concentrations or temperatures are involved.

Sulfuric Acid

It is safe to say that CSPE performs well in sulfuric acid at concentrations below 50 percent and temperatures below 200 F, and at concentrations below 80 percent and temperatures below 158 F. When concentrated acids are in question (66° Baume) no rule can be set. Some experience has been good and some bad. A field test is necessary. Only temperatures close to room temperature should be considered.

Oils

Animal, vegetable, and mineral oil, have slight to moderate swelling effect on CSPE at room temperature.

Solvents

Resistance to swell is a function of aniline point. Low aniline point hydrocarbons cause more severe swell. Aromatic solvents, aldehydes, and chlorinated hydrocarbons should be avoided. CSPE can be used in aliphatic hydrocarbons and some ketones at room temperature, but

TABLE 1—Chemical Resistances of Chlorosulfonated Polyethylene

Chemical	Remarks	Degrees F	Rating*
Acetic Acid—Glacial...	RT swell 60% in 1 month	RT**	NR
Acetic Acid—Diluted..	Expect less effect than glacial	RT	LR
Acetic Anhydride....		175	R
Acetone..........	RT swell 18% to 27%	RT	NR
Aircraft Synthetic Grease	122 F—equilibrium swell 20%; 212 F—equilibrium swell 30%	212	LR
Aluminum Hydroxide..	Bases have no effect	200	R
Aluminum Salts......	Salts have no effect	200	R
Aluminum Sulfate....	230 to 250 F., hose looked good after 200 hours.	250	R
Ammonia—Liquid....	1 week at RT swells 10%, loses 75% of tensile strength	RT	NR
Ammonium Bisulfate..	240 F—hose is satisfactory in use	240	R
Ammonium Hydroxide.	Bases have no effect	200	R
Ammonium Sulfate....	Salts have no effect	200	R
Amyl Acetate........	RT—equilibrium swell 150%	RT	NR
Amyl Alcohol........	Aliphatic alcohols have no effect	200	R
Amyl Chloride.......	Swells badly	RT	NR
Aniline.............	RT—equilibrium swell varies from 20 to 50%	RT	NR
Aniline Hydrochloride.		RT	LR
Aqua Regia (Fumes)..	Seals are being used successfully in fumes at 125 F	RT	R
Aqua Regia (Liquid)..		RT	LR
Asphalt............	Expect severe swelling	RT	NR
ASTM OIL No. 1....	212 F—equilibrium swell varies from—14% to 17%	212	R
ASTM Oil No. 3....	212 F—equilibrium swell varies from 42% to 220%	212	NR
ASTM Ref. Fuel B...	RT—equilibrium swell 110%	RT	NR
Barium Hydroxide...	Bases have no effect	200	R
Barium Salts........	Salts have no effect	200	R
Beer..............	Magnesia cure	RT	R
Beet Juice..........	Same as for beer	RT	R
Benzene...........	Aromatic hydrocarbons have severe swelling action	RT	NR
Benzene Sulfonic Acid, 10%.......		RT	R
Borax.............		200	R
Bordeaux Mixture....	A mixture of cupric sulfate and lime in water, should have no effect	200	R
Boric Acid..........		200	R
Brine Saturated with chlorine.........		167	LR
Bromine—Liquid Anhydrous........		RT	NR
Butane............	Minor swelling effect	RT	R
Butter............	Very little effect on neoprene at 150 F—use magnesia cure	158	R
Buttermilk.........	Magnesia cure	100	R
Butyl Acetate.......		RT	NR
Butyl Alcohol.......	Aliphatic alcohols have no effect	200	R
Butyraldehyde.......		RT	NR
Butyric Acid........		RT	NR
Cadmium Salts......	Salts have no effect	200	R
Calcium Bisulfite.....	Hose unaffected after 1 month's service	200	R
Calcium Hydroxide...	Bases have no effect	200	R
Calcium Hypochlorite.	Tank lining in 20% bleach satisfactory after 3 years	200	R
Calcium Salts.......	Salts have no effect	200	R
Carbolic Acid (Phenol).		RT	LR
Carbon Dioxide.....		200	LR
Carbon Monoxide....	Expect little or no effect	200	R
Carbon Tetrachloride..	Equilibrium swell over 150% at RT	RT	NR
Castor Oil..........		159	R
Chlorine—Liquid....	MgO cure satisfactory in 3 days at RT	RT	NR
Anhydrous..........	PbO has blown spots		
Chlorine Gas.......	Swells 35% in 14 days at RT. Surface less affected than with other elastomers	RT	NR
Chlorine—Saturated Water...........	Good resistance reported after 3 months held test	RT	LR
Chlorine Dioxide....	Lab and field results inconclusive	RT	LR
Chlorobromomethane.	RT Equilibrium swell 390%	RT	NR
Chloroform.........	Severe swelling expected as on neoprene	RT	NR
Chrome Plating Solutions..........		125	R
Chromic Acid, 10%...	158 F satisfactory	158	R
Chromic Acid, 25-30%.	RT—solution coating satisfactory after 30 days	RT	R
Chromic Acid—50% and up...........	Magnesia cure shows no effect after 216 days at RT	RT	R
Chromium Salts......	Salts have no effect	200	R
Citric Acid.........		RT	R
Citrus Oils.........	Swells 200% in 4 days at RT	RT	NR
Clorox............	See sodium hypochlorite		
Cobalt–Nickel Plating Solution........	Satisfactory for use in 9H bright cobalt nickel at 160 F	160	R
Coconut Oil........		RT	R
Cod Liver Oil.......	Equilibrium sw ll 50% at RT	RT	NR
Copper Plating Solution...........	Unsatisfactory in Eex-X solution at 170-190 F (poisons the solution)	190	NR
Corn Oil...........	Expect moderate swelling at 158 F	158	LR
Cotton Seed Oil.....	RT—equilibrium swell 5-10% 158 F—50-60%	158	LR
Creosote...........	Expect moderate to severe swelling	RT	NR
Cresylic Acid.......	This is a mixture of phenols; moderate swelling at RT; very severe at 158 F	RT	NR
Crude Oil..........	Expect moderate swelling at RT	RT	NR
Cyclohexane........	Equilibrium swell 110% at RT	RT	NR
Cyclohexanol.......	Swells 12% in 4 days at RT	RT	NR
Cyclohexanone......	Equilibrium swell 105% at RT	RT	NR
Diacetone Alcohol....	Swells 12% in 4 days at RT	RT	NR
DDT in Kerosene Solution..........	Would be swollen by the kerosene	RT	LR
Dibutyl Phthalate....	Expect moderate to severe swelling	RT	NR
Dichlorobenzene.....	Swells 350% in 7 days at RT	RT	NR
Dichlorobutene.....	Swells 75% in 3 days at RT	RT	NR
Dichlormethane.....	This is ethylene dichloride; causes severe swelling	RT	NR
Diesel Oil..........	Expect moderate swelling at 158 F	158	LR
Diethyl Ether.......	Swells 50% in 1 day at RT	RT	NR
Diethyl Sebacate.....	Swells 15% in 1 day at RT, 80% in 5 days	RT	NR
Dimethylamine......		RT	NR
Dimethyl Ether.....	Swells 13% in 1 day at RT	RT	NR
Dimethyl Formanide.		284	NR
Dioctyl Phthalate....	Expect moderate severe swelling at RT	RT	NR
Dioctyl Sebacate.....	Swells over 200% at RT	RT	NR
Esso Type A Transmission Fluid..	Equilibrium swell 40% at RT	RT	NR
Ethyl Acetate.......		RT	NR
Ethyl Alcohol.......	0% equilibrium swell at RT	200	R
Ethyl Chloride......	Expect moderate to severe swelling at RT	RT	NR
Ethyl Chloroformate..	Swells 98% in 28 days	RT	NR
Ethylene Dichloride..	Severe swelling at RT	RT	NR
Ethylene Glycol.....	No effect in 14 days at 158 F	200	R
Ethylene Oxide......	Expect moderate to severe swelling	RT	NR
Ferric Chloride (60%).		200	R
Ferric and Ferrous Salts.............	Salts have no effect	200	R
Fluoboric Acid......	Effect should be mild	RT	R
Fluosilicic Acid.....	Tank lining in use at 250 F satisfactory in lab tests	250	R
Formaldehyde, 37%	0% swelling, 28 days at RT, 500% at 158 F	RT 158	R NR
Formic Acid........	Expect only slight effect	RT	R
"Freon-12"***	Swells 12% in liquid in 8 days at RT	RT	R
"Freon-13B1"***	Gains 8% in weight in 14 days at RT	RT	R
"Freon-22"***	Equilibrium linear swell of 8% at RT	RT	R
Fruit juices........	Magnesia cure	RT	R
Fuel Oil...........	Slight to moderate swelling expected	158	LR
Furan.............	Swells 25%, softens, loses strength in 18 hours at RT	RT	NR
Furfural...........	Expect moderate swelling at RT	RT	LR
Gasoline...........	Swells 60% in standard automotive at RT	RT	NR
Gelatin............	Expect little or no effect	200	R
Glucose............	Expect little or no effect	200	R
Glue..............	Expect little or no effect	200	R
Glycerin...........	Expect little or no effect	200	R
Hexane............	Expect only slight swelling	RT	R
Hydraulic Oils......		RT	LR
Hydrobromic Acid....	Expect little or no effect	200	R
Hydrochloric Acid, 10%.........	Coatings unaffected after 28 days at RT Swelling and blistering occur at 158 F	RT 158	R NR
Hydrochloric Acid, 37%.........		RT	R
Hydrocyanic Acid....	Expect very little effect	RT	R
Hydrofluoric Acid, Vapors..........	Duct-lining handling vapors at 250-300 F unaffected in 4½ months	300	R

*Code: NR—No Recommendation; LR—Limited Recommendation; R—Recommended
**RT means Room Temperature
***Du Pont's registered trademark for a refrigerant

TABLE 1 (Continued)

Chemical	Remarks	Degrees F	Rating
Hydrofluoric Acid, 48%		158	R
Hydrofluosilicic Acid	Solution coating shows no effect in concentrated acid after 42 days at RT	RT	R
Hydrogen		RT	R
Hydrogen Peroxide, 90%	Affects decomposition rate of H2O9, although CSPE is unaffected		LR
Hydrogen Sulfide	Coating not discolored in 16 hrs. at RT	RT	R
Ink-Carbitol (Acetate Based)	16% swell in 7 days at RT Best of elastomers tested	RT	LR
Isooctane	Expect slight swelling	RT	R
Isopropyl Acetate	Moderate to severe swelling expected	RT	NR
Isopropyl Alcohol	Aliphatic alcohols have no effect	200	R
Isopropyl Ether	Equilibrium swell 42% at RT	RT	NR
Jet Engine Lube (Turbo Oil 15)	Swells 24% at RT, 248% at 350 F	RT / 212	NR
Jet Fuel	Swells about 100% in JP-4, and JP-5 at RT	RT	NR
Kerosene	Equilibrium swell 65% at RT, 90% at 158 F	RT	NR
Ketchup	Magnesia cure	RT	R
Lacquer & Lacquer Thinner	Expect moderate to severe swelling	RT	NR
Lactic Acid	Expect little or no effect	RT	R
Lard Oil	Swells over 150% at 158 F	158	NR
Lead Salts	Salts have little or no effect	200	R
Lime Water	Little or no effect	200	R
Linseed Oil	Expect light to moderate swelling at RT	RT	LR
Lithium Hydroxide	Bases have no effect	200	R
Lubricating Oil	Swells 21% in SAE-10 Motor Oil in 14 days at 158 F	158	LR
Magnesium chloride	Solution coating on steel shows no effect after 30 days in 30% at 220 F	220	R
Magnesium Hydroxide	Bases have no effect	200	R
Magnesium Salts	Salts have little or no effect	200	R
Manganese Salts	Salts have little or no effect	200	R
Mayonnaise	Magnesia cure	RT	R
Mercury		RT	R
Mercury Salts	Salts have little or no effect	200	R
Methyl Alcohol	No change after 14 days at RT	200	R
Methyl Chloride	Expect severe swelling	RT	NR
Methyl Ethyl Ketone	Equilibrium swell about 100% at RT	RT	NR
Methyl Isobutyl Ketone	Equilibrium swell 141% at RT	RT	NR
Methylene Chloride	Equilibrium swell over 250% at RT	RT	NR
Milk	Magnesia cure	RT	R
Mineral Oil	Swells 12% at RT, 25% at 212 F	RT / 212	R / NR
Mineral Spirits	Expect moderate swelling	RT	LR
Molasses		200	R
Monochlorobenzene	Equilibrium swell 306% at RT	RT	NR
Monomethylamine		RT	NR
Mustard	Magnesia cure	RT	R
Naphtha	Equilibrium swell 65% at RT	RT	NR
Naphthalene	Expect severe swelling	RT	NR
Nickel Plating Solution	OK'd for use in nickel lume bright high speed nickel Sol'n at 140 F	140	R
Nickel Salts	Salts have little or no effect	200	R
Nicotine Salts	Expect little or no effect	RT	R
Nitric Acid, up to 30%		RT / 122 / 158	R / LR / NR
Nitric Acid, 30% to 70%		RT	LR
Nitric Acid, Fuming		RT	NR
Nitrobenzene	Swells 60% in 1 day at RT	RT	NR
p-Nitrochlorobenzene	Swells 10% in 35% water slurry, 48 hours at 95 F. Swells 128% in 100% solvent, 68 hrs. at 150 F	150	NR
Nitroglycerin	Absorbs 1% nitroglycerin in 4 weeks at RT	RT	R
Nitroglycerin Waste Acid	Mixture of nitric and sulfuric acids containing nitroglycerin; sample sticky, inelastic after 15 days at RT	RT	NR
Nitrosyl Chloride	Hose satisfactory after 18 months at 125 F	125	LR
p-Nitrotoluene	Swells over 150% in 35% water slurry at 95 F and in 100% oil at 150 F	RT	NR
Nitrous Acid		RT	R
Oleic Acid	Expect moderate to severe swelling	RT	NR
Oleum	Expect severe attack because of SO3	RT	NR
Olive Oil	Equilibrium swell 40% at RT	RT	LR
Palmitic Acid	Expect moderate swelling	RT	LR

Chemical	Remarks	Degrees F	Rating
Pentane	Aliphatic hydrocarbons have little effect	RT	R
Perchlorethylene (Perclene)	Swells 100% in 1 day at RT	RT	NR
Phenol	Expect moderate swelling at RT, severe at 158 F	RT	NR
Phosphoric Acid, up to 85%	Unaffected in 8 months; continuous immersion at 158 F. Discolors acid at 158 F, not at RT	200	R
Phosphorus Oxychloride	Swells very badly in 19 hours at 140 F	RT	NR
Phosphorus Pentafluoride	Unaffected by dry PF5 gas	RT	R
Phosphorus Trichloride	Swollen 4 times original size in 19 hours at 140 F	RT	NR
Phosphorus Trifluoride	Unaffected by dry PF3 gas	RT	R
Pickling Solution		RT / 122	R / NR
Pitric Acid		RT	R
Polyvinyl Acetate		RT	R
Potassium Dichromate		200	R
Potassium Hydroxide	No effect after 28 days at RT in concentrated KOH	200	R
Potassium Permaganate	Pump diaphragm satisfactory after 1 year intermittent service in solution of permanganate, Phosphoric and sulfuric acid	RT	R
Potassium Salts	Salts have little or no effect	200	R
Propane	Aliphatic hydrocarbons have little or no effect	RT	R
Pyroligneous Acid	Expect minor swelling at RT	RT	R
Rapeseed Oil	Expect moderate swelling at RT	RT	LR
Rosin	Expect slight swelling	RT	R
Sea Water	Solution coatings unaffected in 2 months at RT and 1 month at 158 F	158	R
Shellac	Expect only minor effect at RT	RT	R
Silica Gel		200	R
Silica Oils	Because of low compatibility expect little effect	RT	R
Silver Salts	Salts have little or no effect	200	R
Skydrol	Swells 70% in 28 days at RT 135% in 7 days at 158 F	RT	NR
Soap Sol'n	Coatings used successfully in dishwashers	200	R
Sodium Acetate		200	R
Sodium Chlorate		200	R
Sodium Chloride	Solution coating in 20% NaCl unaffected after 30 days at 220 F	220	R
Sodium Dichromate	Unaffected in 20% after 28 days at RT	200	R
Sodium Ethoxide	In alcohol solution—no effect on sample or liquid	RT	R
Sodium Hydroxide up to 73%	Tank car coating in service 2 years at 280 F	280	R
Sodium Hypochlorite		RT	R
Sodium Peroxide		200	R
Sodium Salts	Salts have little or no effect	200	R
Sodium Sulfide		200	R
Soybean Oil		RT	R
Spindle Oil	Expect light to moderate swelling at RT	RT	LR
SR-6 Fuel	Swells 263% at RT	RT	NR
Stannous Chloride	15% has no effect 7 days at 200 F	200	R
Steam, 20 psi	Swells 15% in 18 days	20 psi	R
Steam, 60 psi	Loses 50% of original tensile in 24 hours	60 psi	NR
Stearic Acid	Expect moderate to light swelling	158	LR
Starch	Expect no effect from starch sol'n	200	R
Stoddard Solvent	Expect no effect	RT	NR
Sugar Solutions		200	R
Sulfamic Acid	Satisfactory resistance at 212 F, in unspecified concentration	212	R
Sulfur Dioxide, Liquid	10% swell in 7 days at RT	RT	LR
Sulfur Dioxide, Gas	Swells rapidly and softens in a few days	RT	NR
Sulfuric Acid, up to 50%		250	R
Sulfuric Acid, 50-80%		158	R
Sulfuric Acid, 66° Baume	May discolor acid	RT	LR
Sulfurous Acid	Should be little or no effect	158	R
Sulfur Trioxide	Severe attack in liquid SO3 in 5 days at 212 F	RT	NR
Tall Oil	Expect slight to moderate swelling	RT	LR
Tannic Acid, 10%	Expect slight effect	RT	R

TABLE 1 (continued)

Chemical	Remarks	Degrees F	Rating	Chemical	Remarks	Degrees F	Rating
Tartaric Acid		200	R	Trimethylamine		RT	NR
Terephthalic Acid (Fumes)		212	R	Triethanolamine	Expect little or no effect	158	R
Tertiary Butyl Anthraquinone		158	LR	Trinitrotoluene	10% weight change after 28 days at RT	RT	R
Tetrabutyl Titanate		RT	R	Trinitrotoluene Vapors	3% weight change after 4 days at 325 F	325	R
Tetraethyl Lead (Blend)	Motor mix with ethylene dichloride and ethylene dibromide, swells 183% at RT	RT	NR	Tung Oil	Expect slight swell at RT	RT	R
Tetraethyl Lead (Oil)	Swells 94% at RT	RT	NR	Turpentine	Equilibrium swell 200% at RT	RT	NR
Tetrafluorethylene		200	R	Urea	Water solutions should have little if any effect	200	R
Tetralin	Expect severe swelling	RT	NR	Urine	Little or no effect	RT	R
Thioglycolic Acid	Should have somewhat more effect than acetic acid	RT	NR	Varnish	Solvents used will cause severe swelling	RT	NR
Tin Salts	Salts have little or no effect	200	R	Vegetable Fats—Oils		RT	R
Titanium Tetrachloride	Swells 56% in 7 days at RT becomes brittle and hard	RT	NR	Vegetable Juices	Expect little or no effect	200	R
Toluene	Equilibrium swell 250% at RT	RT	NR	Vinegar	Expect some effect	200	LR
Toluene Diisocyanates	Swells about 200% at RT and surface embrittles	RT	NR	Vinyl Chloride	Would expect severe swelling	RT	NR
Tributyl Phosphate	Swells 100% to 150% in 7 days at RT	RT	NR	Wagner 21-B Brake Fluid	Equilibrium swell 15% at RT	RT	R
Trichlorethylene	Equilibrium swell about 300% at RT	RT	NR	Water	Sol'n coating unaffected in 28 days at 212 F	212	R
Tricresyl Phosphate	Equilibrium swells of 34% at 158 F and of 60% at RT	RT	NR	Whiskey and Wines	Magnesia cure	RT	R
				Xylene	Swells 160% at RT	RT	NR
				Zinc Salts		200	R

should be tested before recommending at elevated temperatures.

Resistance to Chemical Exposure

Table 1 lists alphabetically over 300 chemical media. CSPE compounds have been tested in these media and ratings determined. The ratings are coded as follows:

R—Recommended. This means that good service may be expected.

LR—Limited Recommendation. Good service may be expected under some circumstances, such as intermittent exposure or periods of short duration. Service testing is advisable.

NR—No Recommendation. Service is likely to be too poor to warrant use or insufficient test data are available to permit a more favorable rating. Often adequate service may be obtained under very special conditions. Specific service testing is suggested.

It should be kept in mind that the information and ratings in the table are not meant for literal interpretation. They are, however, guides for determining when and where to consider using CSPE sheet lining or protective coatings.

These data were developed primarily with sheet linings but they also serve as a guide to the resistance of CSPE coatings.

Application

CSPE compounds are available as coatings and as uncured sheets.

Coverage

Coatings. Normally four coats of about 2-mils each over an appropriate primer are recommended to eliminate the possibility of holidays. Coverage will be a function of solids by volume when ready to apply. An average is about 300-400 sq. ft. per gallon, per mil thickness.

Sheet Lining. Calendered sheet is usually used. A sheet thickness of 1/8 inch to 3/16 inch made by plying up three or more plies at the calender seems to be more or less standard.

Flammability and Toxicity

Coatings. The fumes from the solvent systems for CSPE paints are often both toxic and flammable since they are usually aromatics and/or ketones. The same precautions in handling any such systems should be used in handling CSPE paints.

Sheet Lining. The only fire or toxicity hazard involved is in the application of the priming cement and adhesives as in the application of other sheet lining materials.

Surface Preparation

The adhesion of the lining is dependent on the condition of the surface on which it is applied. For optimum results blasting to white metal and degreasing are essential. It is suggested the recommendations in NACE Pub. 53-I (A Report of TP-6G) be followed.[11]

Priming

Coatings. Some systems require primers while others have so-called built-in primers. Many of the chlorinated rubber type primers used for the elastomer based paints work satisfactory, but may stain colored CSPE paint film. Non-staining primers have been developed.

Sheet Lining. Normally a priming cement and an adhesive cement are necessary for the application of CSPE sheet linings. The system used may vary with the manufacturer or applicator and should take into account the service environment involved. Each manufacturer or applicator usually has specific recommendations for best results with their material.

Application Methods

Coatings. Standard methods of spraying and brushing can be used. The usual advantages of hot spraying are obtained with CSPE paints.

Sheet Lining. Rubber sheet lining techniques apply to CSPE sheet stocks. It is necessary to warm-up some stocks before satisfactory handling and adhesion can be obtained. CSPE sheet which is several weeks old has a tendency to be boardy and dry, making it fairly difficult to handle. Cold storage of sheet stock is good practice when it cannot be used fresh from the calender.

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Atmospheric Corrosion Testing of Metals in Canada*

By E. V. GIBBONS

Introduction

THE HEAVY economic losses that can occur as a result of atmospheric corrosion have resulted in many studies of this problem in different countries. Such an outdoor metals exposure program was begun in Canada during 1950 through the Associate Committee on Corrosion of the National Research Council to provide a better understanding of the behavior of different metals and metal coatings when exposed to different Canadian atmospheres. It was a cooperative venture in that industry members of the Committee provided specimens of the various metals selected to be set out at the sites established and operated by the Division of Building Research.

Metals Exposed

The major architectural and structural metals were chosen for comparison in this study. Among the first metals set out and which have now been exposed more than five years are three types of steel, three stainless steels, two magnesium alloys, a rolled zinc, three aluminum alloys and riveted galvanic couples of the aluminum 3S alloy to mild steel, to zinc and to copper. More recently sheet copper, Muntz metal, and two types of sheet lead have been added. Metal coatings on steel of hot-dipped galvanizing, electroplated zinc, sprayed zinc, sprayed aluminum, aluminized steel, and electroplated cadmium have also been exposed. In addition to these metal coatings, a number of different paint systems have been applied to two types of steel and set out at the sites.

Exposure Sites

The exposure sites of the Council and their facilities have already been described.[1] In view of the behavior of the various metals exposed at these different sites, however, the following is a brief description of their location and atmosphere for which each is considered typical.

(1). Ottawa—rural, high humidity; located on the Montreal Road property of N.R.C.

(2). Saskatoon—rural, low humidity; approximately two miles northeast of the campus of the University of Saskatchewan.

(3). Montreal—industrial; located on the roof of a two-story stores building of the Canadian National Railways, in the Point St. Charles district.

(4). Halifax — marine-industrial; located on the roof of a federal public building in the downtown area of the city, two blocks from the harbor.

About the Author

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(5). York Redoubt, N.S.—marine; about seven miles from Halifax. The area used is at an elevation of 100 ft. and is 300 ft. from the ocean.

(6). Norman Wells, N.W.T.—a far northern site; located in the Mackenzie River Valley, approximately 50 miles south of the Arctic Circle.

(7). Rocky Point, B.C.—marine; about fifteen miles from the City of Victoria on Vancouver Island. It is at an elevation of 50 ft. and approximately 1500 ft. from the ocean.

(8). Trail, B.C.—this is a semi-industrial site of the Consolidated Mining and Smelting Company of Canada Limited, which was made available to the committee for corrosion studies. It is located in the Columbia River Valley about six miles north of Trail.

Site Facilities and Related Studies

The sites were provided with tubular racks and stainless steel frames for mounting the specimens. All metal specimens were 4 by 6 inches in size and were held in place by porcelain insulators, at 30 degrees to the horizontal and facing south. Twelve specimens of each type of metal were set out initially at each site. This enabled three specimens of each type to be removed after exposure periods of one, two, five and ten years. The procedure was followed of having the suppliers of the metal prepare the specimens, weigh and identify them by a drilled hole system. This information was checked by the Division prior to shipment to the sites for exposure.

Abstract

The atmospheric corrosion resistance of metals is evaluated after exposure in a number of differing Canadian environments. Test sites included rural, industrial, marine-industrial, marine, far northern and semi-industrial. Metals exposed include three aluminum alloys, aluminum coupled metals, carbon steel, copper-bearing low carbon steel, low alloy copper-nickel-bearing steel, three stainless steels, two magnesium alloys, and rolled zinc. Test exposure periods varied from one to ten years. 2.2.2

After completing a prescribed period of exposure the particular lot of specimens was returned to the Division to be photographed and sent to the supplier for a detailed examination and assessment.

To assist in obtaining a better understanding of the behavior of the various metals a number of environmental factors were measured at the different sites. As all the sites are near weather stations of the Meteorological Division of the Department of Transport, records were available for each site of the precipitation, temperature, hours of sunshine, wind velocity and direction. Since 1954 the relative level of atmospheric sulfur dioxide has been measured monthly. An indication of the seasonal variation of the level of this pollutant and its variation from site to site is shown in Figure 1. Details concerning the measurement of sulfur dioxide and chlorides in the Halifax area have been described previously.[2]

Specimens of mild steel and a standard rolling grade zinc have been exposed for several one-and two-year periods at each of the sites. These specimens were made available by an ASTM subcom-
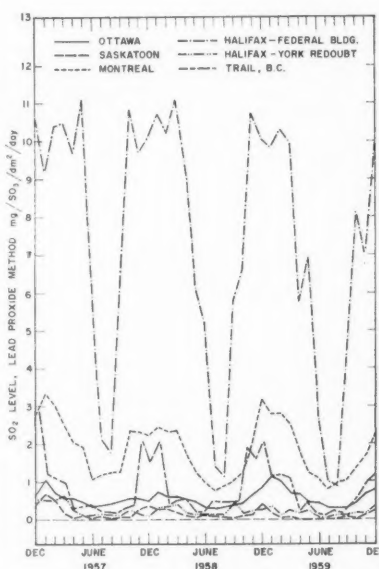
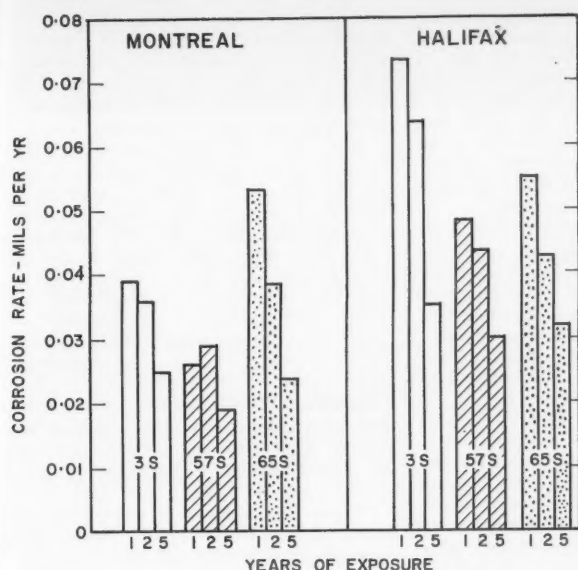Figure 1—Annual variation in SO₂ level at sites.

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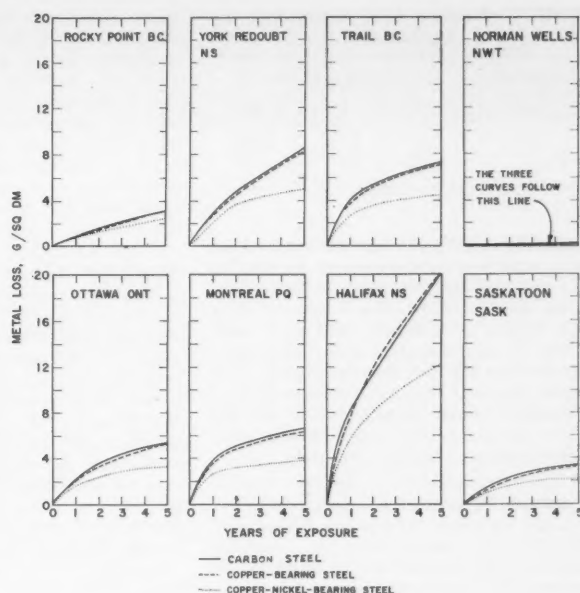Figure 2—Atmospheric corrosion rates for three aluminum alloys.

Figure 3—Time-corrosion curves for steel alloys.

TABLE 1—Analysis of Metals Tested, Percent

| | Aluminum Alloys | | | In Al Couples | | | Steel Alloys | | | Stainless Steel | | | Magnesium Alloys | | Rolled Zinc |
| | | | | Mild Steel | Zinc | Copper | | | | | | | | | |
Element	3S	57S	65S	Desig. 1010			Carbon	Cu Bearing	Cu-Ni Bearing	302	430	316	AZ80	ZK61	
Cu	0.03	0.02	0.36	....	....	99.83	0.090	0.205	0.738	....	....	....	0.020	0.001	0.001
Fe	0.40	0.25	0.64	....	0.40	....	....	....	....	....	....	....	0.003	0.001	0.004
Mg	....	2.25	1.06	....	....	....	....	....	....	....	....	....	....	....	....
Mn	1.06	0.10	....	0.43	....	....	0.29	0.32	0.78	1.24	0.43	1.85	0.26	0.004	....
Si	0.10	0.10	0.64	0.019	....	....	0.002	0.002	0.021	0.41	0.41	0.38	0.06	....	....
Ti	0.014	0.02	0.05	....	....	....	....	....	....	....	....	....	....	....	....
Cr	....	0.26	0.22	....	....	....	....	....	....	18.78	16.62	16.92	....	....	....
C	....	....	....	0.08	....	....	0.064	0.069	0.124	0.12	0.11	0.09	....	....	....
B	....	....	....	0.045	....	....	....	....	....	....	....	....	....	....	....
P	....	....	....	0.014	....	....	0.013	0.014	0.095	0.029	0.030	0.028	....	....	....
Pb	....	....	....	....	1.120	....	....	....	....	....	....	....	0.003	....	0.08
Cd	....	....	....	....	0.041	....	....	....	....	....	....	....	....	....	0.002
Zn	....	....	....	....	98.71	....	....	....	....	....	....	....	0.38	5.9	99.91
Ni	....	....	....	....	....	....	....	....	0.680	6.8	0.75	12.82	0.001	0.001	....
S	....	....	....	....	....	....	0.035	0.048	0.032	0.018	0.025	0.020	....	....	....
Mo	....	....	....	....	....	....	....	....	....	0.23	....	2.43	....	....	....
Al	....	....	....	....	....	....	....	....	....	....	....	....	8.1	....	....
Zr	....	....	....	....	....	....	....	....	....	....	....	....	....	0.83	....
Sn	....	....	....	....	....	....	....	....	....	....	....	....	0.001	....	....
Ca	....	....	....	....	....	....	....	....	....	....	....	....	0.001	....	....

mittee determining the relative corrosivity of the atmosphere at ASTM exposure sites. A correlation of the corrosiveness at eight Canadian sites with the eleven sites in the U.S.A. is available.[3] In the report describing this calibration study the corrosivity at the Ottawa site with respect to steel is the same as the U.S. site at Pennsylvania State University which was taken as unity but it is more corrosive with respect to zinc (1.3 to 1). The site at Norman Wells was the least corrosive of the nineteen sites reported.

The current studies of a task group of ASTM Committee B-3 on the measurement of atmospheric factors affecting corrosion are of special interest. This work has resulted in the development of instrumentation to detect surface moisture and record the time-of-wetness on exposed metal surfaces in which the

Division of Building Research has played a leading part.[4] More recently field instruments of this type have been installed to measure time-of-wetness at three Canadian sites and four ASTM sites to obtain a correlation of the metal loss with time-of-wetness, temperature and pollution.

Exposure Results

A progress report has been published which describes the corrosion behavior after one- and two-year periods of exposure of a number of the metals mentioned previously.[5] A similar report including the results of these metals after five years of exposure is being prepared. Since details of the performance of individual panels and lots are contained in these reports only a brief résumé of the different metals that have completed up to five years of exposure is given here.

The chemical composition of each is shown in Table 1.

Aluminum Alloys

Three aluminum alloys were exposed: 3S-H14, 57S-H34, and 65S-T6. Riveted couples of 3S aluminum sheet and copper, zinc and mild steel were also included.

In general appearance the three alloys were similar at each location. This applies to both the groundward and skyward sides, with few exceptions when examined at the end of the one-, two- and five-year exposure periods. They varied greatly however depending upon the particular sites at which they were exposed. Weathering took the form of surface roughening due to pitting; its extent increased with aggressiveness of the atmosphere. The differences in corrosion rates among the three alloys were

TABLE 2—Stainless Steel Exposed at the Halifax Site

Exposure Period, Years	Weight Loss, gm		
	302	316	430
1	0.132	0.074	0.425
2	0.223	0.165	0.599
5	1.128	0.417	1.144

generally small and up to the end of two years were considered to be similar. By the end of five years of exposure, alloy 57S showed better resistance than the others at the industrial sites with alloy 3S being superior at the mild rural sites. Alloy 65S was intermediate in most cases. Figure 2 shows the corrosion rates, calculated from weight losses, of the three aluminum alloys at the two most corrosive sites—Halifax and Montreal.

The riveted bimetallic couples of copper or mild steel to aluminum 3S alloy caused galvanic corrosion. This was found to be most severe in a marine atmosphere, less severe in industrial atmospheres and negligible at rural sites. Zinc, when coupled to aluminum, tended to protect it in all atmospheres.

Steel

Three steels, a carbon steel, a copper-bearing low carbon, and a low alloy copper-nickel-bearing steel were exposed at each of the sites. The low alloy copper-nickel-bearing steel gave the greatest resistance to atmospheric corrosion at all sites except Norman Wells. The loss due to corrosion at this site is extremely low, however, for all of the metals exposed, as is the weight loss difference between the three steels. There was little difference in weight loss between the carbon steel and the copper-bearing steel. The latter showed a slightly improved resistance at all of the sites after one year of exposure. This behavior continued during the two-and five-year exposure periods. The loss in weight with time of these three steels at each of the sites is shown in Figure 3. These results are somewhat at variance with results reported by others who have had atmospheric corrosion resistance improved by as much as four times for a copper-bearing steel compared to steels with residual copper.[6] It should be noted in Table 1 that the Cu content of the carbon steel is 0.09 percent, which is relatively high. As was found with the aluminum alloys, there was a decrease in the corrosion rate with time for each of the three steels exposed.

Stainless Steels

Three stainless steels, Types 302 and 316 each with a 2B finish and Type 430 with a 4B finish were set out at each of the sites. Their behavior in appearance and weight loss at each of the sites was similar except for alloy 430 at the Halifax site. Here this alloy had a much higher weight loss than 316 and about the same loss as 302 after five years of exposure. The weight loss after one, two and five years at this site for the three alloys is shown in Table 2. These results

show that Type 316 had the least loss after five years. At all of the remaining sites there was very little loss in weight after five years of exposure for any of the three types. As an example of the effect of environment of the Halifax site on Type 430 the metal loss after five years of exposure was found to be 1.144 gm. At the next most corrosive site this same alloy had a loss of 0.011 gm during the same period of exposure.

Magnesium Alloys

The two magnesium alloys exposed, AZ80 and ZK61, were supplied in a chrome pickled condition. Of the two, ZK61 showed considerably less corrosion resistance at all of the sites for each period of exposure. In comparison with the behavior of the other metals, in which their corrosion rates decreased with time, the weight loss for the two magnesium alloys was approximately proportional to the time of exposure. The marine sites were quite corrosive to the ZK61 alloy. The AZ80 alloy showed considerably improved resistance in these areas with the exception of Halifax where a small improvement was found.

Rolled Zinc

The corrosion rate of the rolled zinc varied considerably between sites; the highest rate was at Halifax followed in order by Montreal, Trail, and York Redoubt. Halifax was also found to be considerably more corrosive to the ASTM zinc specimens than any of the ASTM sites.[3] The five-year exposure results have shown that decreases in the rates of corrosion from the one- and two-year results have occurred at the Saskatoon, Halifax, York Redoubt, Norman Wells and Rocky Point sites. They also show increases in rates for the Ottawa and Montreal sites.

The corrosion rate decrease at Halifax may be attributable to the protective action of the relatively heavy deposit that built up on the panels. At the other sites where a decrease in rate has occurred this may be due to the protective action of the corrosion products formed and which remained *in situ*. The increases in rates at Ottawa and Montreal could be due to an increase in aggressiveness of the atmosphere and/or exposure to greater amounts of precipitation. This would tend to wash away corrosion products formed and reduce their protective action. The meteorological records indicate that the annual precipitation at Ottawa and Montreal is greater than at all other sites except for the two in the Halifax area.

Examination of the panels after cleaning indicated that corrosion was substantially uniform and the corrosion appeared to be more severe on the skyward faces than on the groundward.

Conclusions

In all cases the Halifax industrial-marine site was by far the most corrosive of all the sites. Montreal, Trail and York Redoubt were considerably less corrosive and the metal loss at these sites in many instances similar. These sites were fol-

lowed in order by Ottawa, Saskatoon and Rocky Point; Norman Wells was found to have the least corrosive atmosphere. The aggressiveness of the Halifax site is attributable in part to the high level of atmospheric sulfur dioxide which influences the rate of corrosion.

The corrosion performance of the various metals indicated that the penetration rate of the stainless steel alloys was the lowest for the three different exposure periods. Almost no corrosion took place with these alloys except at the Halifax site. The aluminum alloys were the next lowest followed by the rolled zinc. Except for the two Halifax area sites magnesium alloy AZ80 showed better corrosion resistance than the three steel alloys. The copper-nickel-bearing alloy showed considerably better corrosion resistance than the ZK61 magnesium alloy with the carbon steel and the copper-bearing in general just slightly better.

The faying surfaces of the 3S aluminum sheet in the lapped bimetallic, riveted joints were protected by zinc but were adversely affected by copper and mild steel.

The rate of corrosion of the different metals almost invariably decreased with time. There were exceptions to this at some locations for rolled zinc and both magnesium alloys.

Finally the results reported enables a comparison to be made of the performance of the different metals under the exposure conditions described. These results must be used with caution however when predicting the life of the metal as a building component. Different environmental factors of atmosphere, orientation and position with other materials may affect their corrosion characteristics. Therefore studies that will provide ways of measuring the effect of the various factors are encouraged so that their performance in service may be predicted with greater certainty.

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Comments by W. A. Mueller, Pulp and Paper Research Institute of Canada, Montreal, Quebec, Canada.

In the first article the authors state that anodic passivation has not yet been previously used in practical control of corrosion, but this statement has been corrected in the second article when referring to anodic protection of alkaline pulping digesters.[1] The maximum current in this application was not 300 as stated by the authors but 1500 amps.[1] It is true that the potential was not automatically controlled; however, it was recorded continuously by means of three calomel cells. And there was an automatic switch to alarm and to switch off the current, if the passive range was not maintained.

During the study of numerous polarization curves[1,2,3] a strong current density, which increases rapidly with increasing potential, has been found in the passive state with respect to iron in alkaline pulping liquors. This current density is caused by reduction-oxidation reactions, such as formation of polysulfides from sulfides. It does not represent anodic dissolution (corrosion of iron). For this reason a high anodic current density does not cause corrosion, and the trans-passive range is not reached in this application. Hence, no potentiostat is required to maintain the required potential for anodic protection of alkaline pulping digesters.

The basic publications on these studies are:—"A Theory of the Electro-chemical Conversion from Active to Passive States[4]" and "A Theory of the Polarization Curve Technique for Studying Corrosion and Electrochemical Protection."[5] In the latter publication the conditions of electrochemical stability are discussed.

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4. W. A. Mueller. *J. Electrochem. Soc.*, 107, No. 3, 157-164 (1960).
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A Laboratory Evaluation of Zinc Anodes in Sea Water by J. A. H. Carson, W. L. M. Phillips, and J. R. Wellington. Corrosion, Vol. 16, No. 4, 171t-177t (1960) April

Comments by J. T. Crennell:

The authors did not find that silicon, in addition to aluminum, had a very notable effect as an "anti-iron" additive to zinc for anodes; it appears that this may have been due to the technique of preparing the alloys.

Our paper which they cite, and a later paper, (Crennell and Wheeler, *Journal App. Chem.* 571 (1958) September), indicate that the silicon acts by combining with the iron originally present and removing it from the melt (as dross) or rendering innocuous any iron that remains, probably as ferro-silicon. It seems likely that in the work of Carson, Phillips and Wellington, the iron was added subsequently to the preparation of the basic alloys; if this were done the silicon could not act as a "scourer" for the iron, as we believe it should. The advantage of the silicon additive in practice is that it is not necessary to start with a low-iron zinc, nor to take special precautions against contamination by iron: the addition of silicon to the melt just before pouring will deal with even quite high iron contents, giving in effect an iron-free anode.

I note with interest, but with some surprise, the author's observation of an optimum iron-content, about 30 ppm with the low-aluminum alloys: this appears to be a significant effect only at the highest current density (2.9 amp/sq.ft.) (see Figure 12) which is in fact much higher than the practical current density, usually about ½ amp per sq ft.

Reply by W. L. M. Phillips, J. R. Wellington and J. A. H. Carson:

The Zn-Al-Si-Fe alloys used in our tests were prepared by first adding Fe to molten zinc and then adding an 87 percent Al-13 percent Si alloy to the molten Zn-Fe alloy. Due to the reaction between Si and Fe noted by Mr. Crennell, some difficulty was experienced in obtaining alloys with the desired high Fe contents. Considerably more Fe had to be added than was required in the finished alloy. Samples taken from the melt at the same time as the anode billets were cast were analysed for total Fe and found to be close to the desired levels. Recent analyses of these alloys by the method of Crennell and Wheeler,[1] show the "harmful iron" to be only a few ppm in all the Zn-Al-Si alloys which we tested. Thus while the main function of the Si addi-

tion is to remove or tie up Fe in the alloy, in our test we endeavored to determine if a Zn-Al-Si alloy anode performed differently than a Zn-Al anode with the same total Fe content. Our results, while not conclusive, indicated that the Si has a very minor effect except in the current variation tests where the Zn-Al-Si alloys showed less polarization at very high current density (Figure 18).

Regarding the observed optimum iron level of 30 ppm in low aluminum alloys, this conclusion is based on the statistical analysis of the results in the second test series (Figure 12) and of the current evidence in the results of the first test series (Figure 12) and of the current density change tests (Figure 18). The differences in potential of alloys with 3 and 32 ppm Fe and the same Al content are marked at 20 ma/in² but are much smaller at 1 to 8 ma/in². While it is true that large zinc anodes usually separate at current densities in this lower range, small cross-section anodes (such as small rods in heat exchangers) can operate at quite high current densities. Further tests may be necessary to determine if the small differences observed at the lower current densities are significant. The important point is that zinc alloys containing 0.3 to 0.6 percent Al can readily tolerate iron contents of 50 ppm or more so that with these alloys the precautions necessary to produce very low iron material are not necessary.

Reference
1. J. T. Crennell and W.C.G. Wheeler. Zinc Alloy Anodes. *Jl. Appl. Chem.*, 8, 571 (1958) Sept.

High Temperature Furnace Corrosion of Type 309 Alloy Steel by R. D. Merrick. Corrosion, Vol. 16, No. 11, 578t-580t (1960) Nov.

Question by Robert W. Manuel, Rye, New York:

How was the composition of the corrosion product calculated? The balance is shown as metallic iron. The analysis as stated is a metal, not a corrosion product.

Reply by R. D. Merrick:

Mr. Manuel is correct in stating that the chemical analysis in Table 3 is presented as a metal rather than as a corrosion product. This analysis was obtained to determine the quantity of certain metals in the corrosion product which were believed to influence the corrosion experienced.

Question by J. M. Bialosky, Koppers Co., Inc., Verona, Pa.:

Do you know the molybdenum content of the alloys used?

Reply by R. D. Merrick:

The molybdenum content of the alloys mentioned was not determined.

Question by John J. Moran, The International Nickel Co., Inc., New York, N. Y.:

Although TiO₂ may have contributed to the lowering of the fusion point of the deposit in the service failure, this material was not present in the pilot plant test and the fusion point was still within the service temperature range. Do you have any analysis of the deposit in this case or any comment as to the cause of the lowered fusion temperature when TiO₂ is not present?

Reply by R. D. Merrick:

No analysis of the corrosion product from the pilot plant exposure was made. However, Mr. Moran is correct in stating that TiO₂ was most likely not present. In subsequent pilot plant exposures it was possible to initiate the formation of tubercules by operating with reducing conditions. From this, the necessity of a "foreign" material, such as TiO₂, is not now considered necessary for the attack to initiate.

Practicality of Establishing Threshold Values to Eliminate Stress Corrosion Failures in Metals and Alloys, by Henry Suss. Corrosion Vol. 17, 61t-66t (1961) Feb.

Question by Glenn R. Roberson, Standard Oil Co. of Texas, Houston, Texas:

Would a Monel sheath function the same as a chrome plating in the example. In other words, would stress corrosion cracking be accelerated by a fault in the monel?

Reply by Henry Suss:

Yes, if Monel is cathodic to the material covered by it.

Additional Comment by R. L. Bob McGlasson, Continental Oil Company, Ponca City, Okla.:

Cracking would not be accelerated by the Monel if the cracking were a function of the presence of hydrogen sulfide.

Question by R. F. Weeter, Midland, Texas:

You mentioned that 2 parts per million of oxygen was more detrimental than 30 to 40 ppm. Did you investigate the effect of lower concentrations?

Reply by Henry Suss:

The presence of 0.5 to 2 ppm oxygen in 300 F ± 5 F high purity waters will produce a more corrosive environment and an accelerated rate of stress corrosion failures of hardened (RC 36-42) AISI 410 than will 30-40 ppm oxygen. There is no accelerated corrosion attack if the oxygen content is less than 0.1 ppm. There are no data on intermediate ranges (0.1 to 0.4 ppm or 2 to 30 ppm). It is stressed that the above data are applicable only to hardened AISI 410 in 300 F high purity water, and will vary

TABLE 1—Effect of Heat Treatment on the Mechanical Properties of Carborundum Grade 11 Zirconium

Condition	Ultimate Strength, psi	0.2 Percent Offset Yield Strength, psi	Elongation in 1 Inch, Percent	Reduction in Area, Percent	Minimum Bend Radius 180° Bend
Alpha annealed after hot working............	64,400	51,400	23	42	3T
Water quenched............... from 1800 F................	72,900 75,300	52,800 55,800	23 22	49 50	3T 3T
Slow cooled................... from 1800 F................	61,400 61,800	46,700 43,900	23 22	28 28	4T Cracked at 90° on 3T

with changes in temperature or chemistry of the environment, different materials, and the same materials in different metallurgical condition.

Corrosion of Metals by Weak Acids Under Heat Transfer Conditions, by N. D. Groves, C. M. Eisenbrown and L. R. Scharfstein. Corrosion, Vol. 17, 173t-176t (1961) April

Comments by A. L. Thomas, Standard Ultramarine and Color Co., Huntington, West Virginia:

Corrosion rate is a function of surface finish. The surface finish of all sample specimens of different composition must be identical before corrosion rate comparisons can be made. Relative rates of corrosion of two samples of different composition, for example, may be reversed at two different surface finishes. Do the authors intend to make a study of surface finish in order to reduce their data to an absolute scale?

Reply by C. M. Eisenbrown:

The corrosion rate can be initially affected by the surface finish since the rougher the surface, the greater will be the surface area exposed to the corrodent. This could be a factor in conducting corrosion tests where the corrosion rate is low and/or exposure is short and not repeated. However, where the corrosion rate is high, the surface exposed to the corrodent is changing quite rapidly and initial surface roughness loses its significance. For these heat transfer studies, the effect of different surface finishes was not studied; however, all the specimens, whether used as heat transfer surfaces or as immersion coupons, had a 32-microinch RMS finish. This finish was obtained by using a surface grinder. A comparison of this finish with sandblasted, shot-peened, hot rolled or cold rolled finishes was not made.

Intergranular Corrosion of Commercially Pure Zirconium, by B. S. Payne and D. K. Priest. Corrosion, Vol. 17, No. 4, 196t-200t (1961) April.

Question by B. E. Tenzer, Foster Wheeler Corp., New York, N. Y.:

Has any work been done on the time-

temperature dependence of the precipitation of the intermetallics? Specifically, may one expect such precipitation and subsequent corrosion after time at service temperatures?

Reply by B. S. Payne:

The only investigation made on time-temperature dependence of the precipitation of the intermetallics has been in the temperature range 1500-1900 F, near the alpha-beta transformation zone. In these limited studies, time did not appear to be an influencing factor provided that a minimum time was present. This is substantiated by the fact that cooling rate is influential as shown by the water quenched vs. slow cooled samples.

Since this phenomena is directly related to the alpha-beta transformation zone, it does not seem likely that precipitation and corrosion could occur at normal service temperatures. Although it is difficult to specify an exact temperature at which this mechanism occurs, temperatures somewhat below the transformation should not cause a precipitation of intermetallics no matter what the exposure time might be.

Discussion by John H. Schemel, The Carborundum Metals Co., Akron, N.Y.:

Since the work presented in this paper shows an impurity enriched phase at the grain boundaries in the heat affected zone of welds, it seemed in order to determine the mechanical properties of the structures produced in this study. This is shown in Table 1.

Room temperature tensile and bend tests indicate a distinct loss of ductility in structures slow-cooled through the beta to alpha transition. Water quenched samples and annealed samples had minimum bend radii of 3T (sheet would bend 180° around a pin whose radius was three times the sheet thickness) while the sheet slow-cooled from 1800 F cracked when bent 90° around a 3T pin. This loss of ductility was also evidenced in the tensile tests where reduction in area fell from 50 percent for specimens water quenched from the beta field to 22 to 23 percent for the slow-cooled bars. Water quenching resulted in an increase of about 12 percent in the ultimate strength. Slow-cooling lowered the yield strength.

This preliminary study indicates that formability of water quenched sheet should be good because of the wide differential in the yield and ultimate strengths. Slow-cooling through the beta to alpha transformation not only lowers the corrosion resistance, but will embrittle the region near the weld.